An organomercury enzyme activator as a versatile template for new organomercury(II) compounds encompassing homobimetallic (RHg/Hg) and heterobimetallic (RHg/Cd) compositions: Syntheses, photoluminescence and structures

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$ligandprecursor, 2-[(4-chloromercuryl)phenyl)iminomethyl]pyridine(15)withHgCl$2, $followedbycrystallizationfrom$
$HgorCd)whencrystallizedfromDMF.Thesereactionsgaveaccesstonovelbimetallicimine functionalizedchloro-$
$compounds.Thecompoundswerecharacterizedbyelementalanalysis, andIRand1HNMRspectroscopicstudies.Thesolutio$
$functionalizedorganomercurycompound$(3)2, $apolymericorganomercurio-ligand(15)n, homobimetallicorganomercury$

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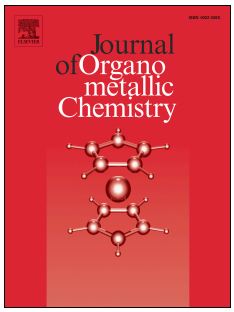

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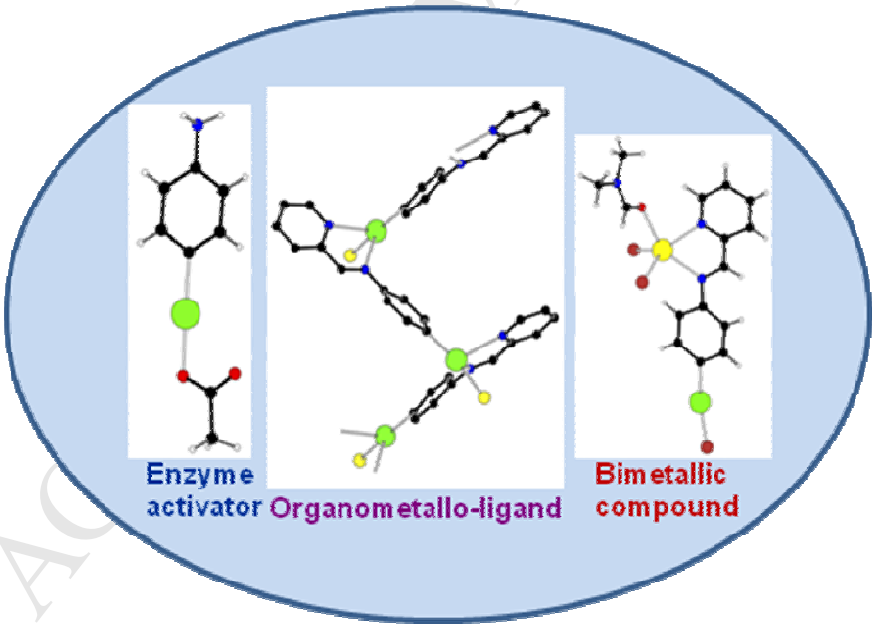

Construction of mono- and a bi-metallic organomercury/mercury and organomercury/cadmium compounds were accomplished from an enzyme activator via suitably designed imine-functionalized organomercury ligand.

An organomercury enzyme activator as a versatile template for new organomercury(II) compounds encompassing homo-bimetallic (RHg/Hg) and hetero-bimetallic (RHg/Cd) compositions: Syntheses, photoluminescence and structures

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ABSTRACT

A series of pale yellow imine-functionalized acetyloxy(4-(arylideneamino)phenyl)mercury(II) compounds (**2**-**7**) were obtained by the reactions of acetyloxy(4-aminophenyl)mercury(II) (**1**) with arylaldehydes in equimolar ratios in absolute ethanol under reflux conditions. Organomercury compounds **2**-**5** and **7**, when treated with 1,5-diphenylthiocarbazone (dptc) in chloroform, formed dark-red (4-((*E*)-arylideneamino)phenyl)(((*Z*)-((*E*)-phenyldiazenyl)(2-phenylhydrazono)methyl)thio)mercury compounds (**8**-**12**) in alkaline medium. The reaction of **7** with a slight excess of mercuric chloride in anhydrous methanol led to the formation of the bimetallic compound (2-{[4-(acetyloxymercuryl)phenyl]iminomethyl}pyridine-κ^2N,N')dichloromercury(II) (**7**.$HgCl_2$ = **13**). Homobimetallic compound **18** can be obtained from the reaction of the organomercurio-ligand precursor, 2-[((4-chloromercuryl)phenyl)iminomethyl]pyridine (**15**) with $HgCl_2$, followed by crystallization from DMSO. Analogous DMF adducted mercury(II) and cadmium(II) compounds, **19** and **20,** were also synthesized from the reaction of (**15**) with MCl_2 (M = Hg or Cd) when crystallized from DMF.

These reactions gave access to novel bimetallic imine-functionalized chloro- compounds. The compounds were characterized by elemental analysis, and IR and ^{1}H NMR spectroscopic studies. The solution state photophysical properties are also reported. The crystal structures of a polymeric organomercury compound $(\mathbf{1})_n$, a dimeric imine-functionalized organomercury compound $(\mathbf{3})_2$, a polymeric organomercurio-ligand $(\mathbf{15})_n$, homobimetallic organomercury/mercury mixed compounds $(\mathbf{18})_n$ and $(\mathbf{19})_n$, and a heterobimetallic organomercury/cadmium mixed compound $(\mathbf{20})_n$ are reported along with their supramolecular motifs.

Keywords: organomercury, homobimetallic compounds, heterobimetallic compounds, metallo-*N,N'*-donor ligand, spectroscopy, crystal structure

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1. Introduction

The chemistry of organomercury compounds is one of the well-studied areas in organometallic chemistry and their co-ordination and structural aspects are also well documented [1-2]. The early development of organomercurial chemistry as compared to other organometallic compounds can be attributed to the high stability of organomercury compounds to air and moisture. Despite high toxicity, organomercury compounds accommodate all functional groups and their remarkable chemical and thermal stability have made them particularly attractive as synthetic intermediates [3]. In recent years, organomercury compounds have also attracted attention as very soft and versatile reagents for palladium catalyzed cross-coupling reactions [4] and transmetallating agents [5-7]. In addition, organomercury(II) compounds of 1,5-diphenylthiocarbazone (a N,S-donor ligand, dptc) have been investigated for their yellow ↔ blue photochromism properties [8,9]. The crystal structures of such photochromic organomercury(II) compounds were also investigated and they exhibited planar, irregular three-coordination T-shaped geometries at the mercury atom [10]. Secondary bonding interactions involving mercury and heteroatom(s) continue to draw considerable attention due to their crucial role in template-free synthesis of mercuramacrocycles [11,12]. Furthermore, the supramolecular chemistry of organomercury 1,1-dithiolates, incorporating uninegative ligands involving dithiocarbamate ($^{-}S_2CNR_2$), xanthate ($^{-}S_2COR$) and dithiophosphate ($^{-}S_2P(OR)_2$), is well-developed and continues to attract attention owing to the diversity of supramolecular motifs [13-23]. While the Cambridge Structural Database (version 1.16 with February 2014 updates [24]) contains data for 157 structures of organomercury(II) complexes with carboxylate ligands, few reports analyze and discuss the supramolecular structures of these materials [25]. The organomercury chemistry of aminobenzoates is particularly attractive, since they exhibit supramolecular assemblies owing to the presence of donor NH_2 groups *e.g.* ((2-

aminobenzoyl)oxy)(2,5-dimethylphenyl)mercury(II) [25]. Secondly, these can be used as a precursor for synthesizing new compounds with novel supramolecular features, as observed in (*E*)-((2-((3-formyl-4-hydroxyphenyl)diazenyl)benzoyl)oxy)(phenyl)mercury(II) and (*E*)-(2,5-dimethylphenyl)((2-((3-formyl-4-hydroxyphenyl)diazenyl)benzoyl)oxy)mercury(II) [25]. Organomercury Lewis acid-base compounds containing two amino groups *e.g.*, bis(4-amino-2,3,5,6-tetrafluorophenyl)mercury(II) also provide the opportunity to build two-dimensional supramolecular chain structures [26].

On the other hand, metallamacrocycles incorporating mercury have also been studied extensively [27-33]. Among these, the polydentate organomercury macrocycles have attracted considerable current interest. The organomercury macrocycles include trimeric-perfluoro-*o*-phenylenemercury [27], [9]mercuracarborand-3 [28], [12]mercuracarborand-4 [28], a 24-membered macrocyclic perfluoroglutarate derivative [29a,b] and a cyclic pentameric $[(CF_3)_2CHg]_5$ macrocycle [30]. Due to the electrophilic nature of the metal ions, mercuramacrocycles act as sensors [31], catalysts [32], and anion receptors [33]. The binding of electron-rich species, e.g., anions [28-33], solvent molecules, arenes, and alkynes with Lewis acidic mercuramacrocycles has been extensively investigated by Gabbaï and co-workers and others [34,35].

Besides industrial applications and academic interests on mercury compounds, acetyloxy(4-aminophenyl)mercury(II) (**1**: compound of present investigation) is frequently being used as an activator to achieve enzyme activity by the dissociation of an enzyme-inhibitor compound to give the free enzyme [36,37]. Although organomercury compound **1** has been known for a long time [38-40], its crystal and molecular structure is not known. We therefore began with the determination of the crystal structure of **1** and then studied its condensation reactions to afford various imine-functionalized acetyloxy(4-(arylideneamino)phenyl)mercury(II) compounds (**2**-**7**). Compounds **2**-**5**

and **7** were also reacted with dptc which provided new mercury derivatives (**8-12**), as shown in Scheme 1(ii). Further, a new organomercurio-*N*,*N*'-donor ligand (**15**) has been synthesized and its reactions with MCl_2 (M = Hg, Cd) resulted in the formation of homobimetallic compounds **18** and **19**, and heterobimetallic compound **20,** upon recrystallization from suitable donor solvents. Synthetic avenues towards the preparation of the aforementioned compounds are detailed in Scheme 1. Representative examples of the synthesized organomercury(II) compounds, such as $(\mathbf{3})_2$, 2-[((4-chloromercuryl)phenyl)iminomethyl]pyridine $(\mathbf{15})_n$, bimetallic compounds (RHg/Hg) **18** and **19,** and (RHg/Cd) **20** have been structurally characterized in the solid state by single-crystal X-ray diffraction; the photophysical properties of these compounds in solution are also reported.

2. Experimental

2.1. Materials

Caution! *Compounds of mercury are highly toxic* [41]. *Care must be taken when handling samples, and appropriate disposal procedures are necessary.* All chemicals were used as purchased without purification: benzaldehyde (Sarabhai Chemicals), 2-hydroxybenzaldehyde, 4-dimethylaminobenzaldehyde, mercuric chloride, 1,5-diphenylthiocarbazone, pyridine-2-carbaldehyde (Merck), 4-methoxybenzaldehyde (Sisco), 4-hydroxybenzaldehyde (Sd Fine), and mercuric acetate (Loba chemicals), except aniline (Sd Fine) which was freshly distilled prior to use. Solvents were purified by standard procedures and were freshly distilled prior to use.

2.2. Physical measurements

Melting points were recorded in capillary tubes on a Scanca apparatus and are uncorrected. Elemental analyses were performed using a Perkin Elmer 2400 series II instrument. IR spectra in the range 4000-400 cm^{-1} were obtained on a Perkin Elmer Spectrum BX series FT-IR spectrophotometer

with samples investigated as KBr discs. The ^{1}H NMR spectra were recorded on a Bruker Avance II spectrometer and measured at 400.13 MHz. The ^{1}H chemical shifts were referenced to Me_4Si set at 0.00 ppm. Steady-state absorption spectra were recorded at ambient temperature in acetonitrile (spectroscopy grade, Merck) solution on a Perkin-Elmer model Lambda25 absorption spectrophotometer. Fluorescence spectra were obtained in a Hitachi model FL4500 spectrofluorimeter (with the excitation and emission slits fixed at 10 and 20 nm, respectively) and all the spectra were corrected for the instrument response function. Quartz cuvettes of 10 mm optical path length received from Perkin Elmer, USA (part no. B0831009) and Hellma, Germany (type 111-QS) were used for measuring absorption and fluorescence spectra, respectively.

2.3. Synthesis of organomercury compounds

*2.3.1. Synthesis of acetyloxy(4-aminophenyl)mercury(II) (**1**)*

Compound **1** was prepared from aniline and mercury(II) acetate according to published method [3] with some modification. To an aqueous suspension of $Hg(OAc)_2$ (5.0 g, 15.688 mmol) in 25 mL of water, 2.9 mL (2.96 g, 31.783 mmol) of freshly distilled aniline was added under stirring conditions, whereupon a clear solution was formed initially followed by the rapid formation of a white precipitate. The stirring was continued for 3 h at ambient temperature and then the mixture was filtered. The residue was washed with water (3 x 5 mL), acetone (3 x 5 mL) and dried *in vacuo*. The dried solid was dissolved by boiling in acetonitrile and filtered while hot. The filtrate, upon cooling to r.t., afforded white crystalline material. Yield: 55% (4.39 g). M.p.**:** 162-164 °C (166-167 °C [38]; 148 °C [40]). Found: C, 27.38; H, 2.63; N, 4.08%. Calc. for $C_8H_9HgNO_2$: C, 27.30; H, 2.58; N, 3.98%. IR (KBr cm^{-1}): 1628 ν_{as}(OCO). ^{1}H NMR ($CDCl_3$): 7.07 [d, J = 8.0 Hz, 2H, H-2,6], 6.70 [d, J = 8.0 Hz, 2H, H-3,5], 3.79 [br s, 2H, NH_2], 2.09 [s, 3H, CH_3CO_2] ppm.

*2.3.2. Reactions of **1** with arylaldehydes:* Reactions of **1** with appropriate aldehydes yielded acetyloxy(4-(arylideneamino)phenyl)mercury(II) compounds **2**-**7**. The synthetic methodologies are very similar, so that the preparation of (*E*)-acetyloxy(4-(benzylideneamino)phenyl)mercury(II) **2** is given here as a representative case.

*2.3.2.1. Synthesis of (E)-acetyloxy(4-(benzylideneamino)phenyl)mercury(II) (**2**)*

To a hot solution of **1** (0.5 g, 1.421 mmol) in ethanol (40 mL) was added a solution of benzaldehyde (0.15g, 1.413 mmol) in ethanol (2 mL) whereupon the solution turned yellow immediately. The reaction mixture was refluxed for 4 h, which resulted in the formation of a pale yellow precipitate. The solvent was removed on a rotary evaporator and the yellow residue obtained was washed with hexane, filtered and dried *in vacuo*. This dried crude product was dissolved by boiling in 40 mL of acetonitrile and filtered while hot. The filtrate, upon cooling to room temperature, afforded pale yellow crystalline material. Yield: 36% (0.47 g). M.p.: 124-126 °C. Found: C, 41.16; H, 2.90; N, 3.28%. Calc. for $C_{15}H_{13}HgNO_2$: C, 40.94; H, 2.98; N, 3.18%. IR (KBr cm^{-1}): 1624 ν_{as}(OCO), 1603 ν_{as}(C(H)=N). Uv-Vis (CH_3CN): λ_{max} (nm) (ε[M^{-1} cm^{-1}]): 343 (11,724). ^{1}H NMR ($CDCl_3$): 8.35 [s, 1H, CH=N], 7.83 [m, 2H, H-8,12], 7.41 [m, 3H, H-9,10,11], 7.26 [d, J = 8.5 Hz, 2H, H-2,6], 7.14 [d, J = 8.5 Hz, 2H, H-3,5], 2.03 [s, 3H, CH_3CO_2] ppm.

*2.3.2.2. Synthesis of (E)-acetyloxy(4-((2-hydroxybenzylidene)amino)phenyl)mercury(II) (**3**)*

A similar synthetic procedure as for **2** was used, except that benzaldehyde was replaced by 2-hydroxybenzaldehyde, giving yellow crystals from acetonitrile solution. Yield: 58%. M.p.**:** 174-176 °C. Found: C, 39.30; H, 3.05; N, 2.95%. Calc. for $C_{32}H_{34}Hg_2N_2O_8$: C, 39.37; H, 3.51; N, 2.87%. IR (KBr cm^{-1}): 1619 ν_{as}(OCO), 1619 ν_{as}(C(H)=N). Uv-Vis (CH_3CN): λ_{max} (nm) (ε[M^{-1} cm^{-1}]): 315

(7,255). ^{1}H NMR ($CDCl_3$): 8.50 [s, 1H, CH=N], 7.30 [m, 4H, H-2,6,10,12], 7.20 [d, J = 8.5 Hz, 2H, H-3,5], 6.98 [d, 1H, H-9], 6.87 [t, 1H, H-11], 2.03 [s, 3H, CH_3CO_2] ppm. *Note: ^{1}H NMR signals due to OH and coordinated CH_3OH were not detected. These were subsequently confirmed from single crystal X-ray crystallographic data.*

*2.3.2.3. Synthesis of (E)-acetyloxy(4-((4-(dimethylamino)benzylidene)amino)phenyl)mercury(II) (**4**)*

A similar synthetic procedure as for **2** was used, except that benzaldehyde was replaced by 4-dimethylaminobenzaldehyde, giving yellow crystals from acetonitrile solution. Yield: 32%. M.p.: 162-164 °C. Found: C, 42.41; H, 3.55; N, 6.01%. Calc. for $C_{17}H_{18}HgN_2O_2$: C, 42.26; H, 3.76; N, 5.80%. IR (KBr cm^{-1}): 1604 ν_{as}(OCO) and ν_{as}(C(H)=N). Uv-Vis (CH_3CN): λ_{max} (nm) (ε[M^{-1} cm^{-1}]): 357 (23,636). ^{1}H NMR ($CDCl_3$): 8.20 [s, 1H, CH=N], 7.68 [d, J = 8.5 Hz, 2H, H-8,12], 7.22 [d, J = 8.5 Hz, 2H, H-2,6], 7.11 [d, J = 8.5 Hz, 2H, H-3,5], 6.65 [d, J = 8.5 Hz, 2H, H-9,11], 2.98 [s, 6H, $N(CH_3)_2$], 2.03 [s, 3H, CH_3CO_2] ppm.

*2.3.2.4. Synthesis of (E)-acetyloxy(4-((4-methoxybenzylidene)amino)phenyl)mercury(II) (**5**)*

A similar synthetic procedure as for **2** was used, except that benzaldehyde was replaced by 4-methoxybenzaldehyde, giving pale yellow crystals from acetonitrile solution. Yield: 38%. M.p.: 160-162 °C. Found: C, 40.95; H, 3.35; N, 3.10%. Calc. for $C_{16}H_{15}HgNO_3$: C, 40.88; H, 3.22; N, 2.98%. IR (KBr cm^{-1}): 1621 ν_{as}(OCO), 1605 ν_{as}(C(H)=N). Uv-Vis (CH_3CN): λ_{max} (nm) (ε[M^{-1} cm^{-1}]): 316 (20,190). ^{1}H NMR ($CDCl_3$): 8.25 [s, 1H, CH=N], 7.74 [d, J = 8.5 Hz, 2H, H-8,12], 7.22 [d, J = 8.5 Hz, 2H, H-2,6], 7.10 [d, J = 8.5 Hz, 2H, H-3,5], 6.89 [d, J = 8.5 Hz, 2H, H-9,11], 3.78 [s, 3H, OCH_3], 2.00 [s, 3H, CH_3CO_2] ppm.

*2.3.2.5. Synthesis of (E)-acetyloxy(4-((4-hydroxybenzylidene)amino)phenyl)mercury(II) (**6**)*

A similar synthetic procedure as for **2** was used, except that benzaldehyde was replaced by 4-hydroxybenzaldehyde, giving bright yellow crystals from acetonitrile solution. Yield: 33%. M.p.: >250 ^{o}C. Found: C, 39.66; H, 3.00; N, 2.89%. Calc. for $C_{15}H_{13}HgNO_3$: C, 39.50; H, 2.88; N, 3.07%.IR (KBr cm^{-1}): 1603 ν_{as}(OCO) and ν_{as}(C(H)=N). Uv-Vis (CH_3CN): λ_{max} (nm) (ε[M^{-1} cm^{-1}]): 321 (11,005). ^{1}H NMR (DMSO-d_6): 9.75 [s, 1H, CH=N], 7.73 [d, 4H, H-8,9,11,12], 6.89 [d, 4H, H-2,3,5,6], 1.91 [s, 3H, CH_3CO_2] ppm. The signal for phenol was exchanged due to the presence of water in the solvent.

*2.3.2.6. Synthesis of (E)-acetyloxy(4-((pyridin-2-ylmethylene)amino)phenyl)mercury(II) (**7**)*

A solution of pyridine-2-carbaldehyde (0.15 g, 1.40 mmol) in ethanol (2 mL) was added to a hot solution of **1** (0.5 g, 1.421 mmol) in ethanol (40 mL) whereupon the solution turned yellow immediately. The mixture was stirred at ambient temperature for 4 h, which resulted in the formation of a yellow precipitate. The mixture was filtered and the residue washed with hexane (3 x 5 mL) and dried *in vacuo*. The dry residue was dissolved by boiling in chloroform, filtered while hot and concentrated to one-fourth of its original volume. The product was precipitated from hexane, filtered and dried *in vacuo.* Several recrystallizations from chloroform-hexane mixtures yielded a bright yellow product in 62% (0.40 g) yield. M.p.: 150-152 °C. Found: C, 38.66; H, 3.80; N, 6.49%. Calc. for $C_{14}H_{12}HgN_2O_2$: C, 38.12; H, 2.74; N, 6.36%. IR (KBr cm^{-1}): 1623 ν_{as}(OCO) and ν_{as}(C(H)=N), 1598, 1480, 1435 ν(C=N)py. Uv-Vis (CH_3CN): λ_{max} (nm) (ε[M^{-1} cm^{-1}]): 322 (11,309). ^{1}H NMR ($CDCl_3$): 8.77 [d, J = 5.0 Hz, 1H, H-9], 8.57 [s, 1H, CH=N], 8.18 [d, J = 8.0 Hz, 1H, H-12], 7.83 [t, 1H, H-11], 7.20-7.45 [m, 5H, rest of the protons], 2.10 [s, 3H, CH_3CO_2] ppm.

*2.3.3. Reactions of acetyloxy(4-(arylideneamino)phenyl)mercury(II) (**2-7**) with dptc:* The preparations of compounds **8**-**12** are very similar, so that the preparation of (4-((*E*)-benzylideneamino)phenyl)(((*Z*)-((*E*)-phenyldiazenyl)(2-phenylhydrazono)methyl)thio)mercury(II) (**8**) is given here as a representative case.

*2.3.3.1. Synthesis of (4-((E)-benzylideneamino)phenyl)(((Z)-((E)-phenyldiazenyl)(2-phenylhydrazono)methyl)thio)mercury(II) (**8**)*

To a solution of **2** (0.25 g, 0.568 mmol) in chloroform (15 mL) was added a solution of dptc (0.14 g, 0.546 mmol) in chloroform (10 mL) under stirring condition whereupon the solution turned dark red immediately and the stirring was continued for an additional 30 min. Then NH_4OH solution (50 mL, 1M) was added drop-wise to the reaction mixture and the stirring was continued for an additional 30 min. The reaction mixture was transferred to a separating funnel and shaken for 5 min. whereby the two phases were separated. The organic layer was washed several times with water until neutral, dried over anhydrous sodium sulphate and filtered. The filtrate was concentrated and precipitated from hexane and this process was repeated at least thrice. The dark-red precipitate was filtered and dried *in vacuo*. The residue was recrystallized from a chloroform-hexane mixture which yielded red microcrystalline material. Yield: 62% (0.24 g). M.p.: >250 °C. Found: C, 48.90; H, 3.53; N, 10.88%. Calc. for $C_{26}H_{21}HgN_5S$: C, 49.08; H, 3.33; N, 11.01%. IR (cm^{-1}): 1614 ν(C=N)dpt and ν_{as}(C(H)=N), 1434 ν(N=N), 688 ν(C-S). ^{1}H NMR ($CDCl_3$): 9.22 [br s, 1H, NH], 8.48 [s, 1H, CH=N], 6.80-8.00 [m, 19H, ArH] ppm.

*2.3.3.2. Synthesis of (4-((E)-(2-hydroxybenzylidene)amino)phenyl)(((Z)-((E)-phenyldiazenyl)(2-phenylhydrazono)-methyl)thio)mercury(II) (**9**)*

A similar synthetic procedure as for **8** was used, except that **2** was replaced by **3**, giving a dark-red compound. Yield: 36 %. M.p.: 188-190 °C. Found: C, 48.04; H, 3.43; N, 10.58%. Calc. for $C_{26}H_{21}HgN_5OS$: C, 47.87; H, 3.25; N, 10.74%. IR (cm^{-1}): 1618 ν(C=N)dpt and ν_{as}(C(H)=N), 1435 ν(N=N), 688 ν(C-S). ^{1}H NMR ($CDCl_3$): 13.24 [br s, 1H, OH], 9.22 [br s, 1H, NH], 8.65 [s, 1H, CH=N], 6.80-8.00 [m, 18H, ArH] ppm.

*2.3.3.3. Synthesis of (4-((E)-(4-(dimethylamino)benzylidene)amino)phenyl)(((Z)-((E)-phenyldiazenyl)(2-phenylhydrazono)methyl)thio)mercury(II) (**10**)*

A similar synthetic procedure as for **8** was used, except that **2** was replaced by **4**, giving a dark-red compound. Yield: 92%. M.p.: 196-198 °C. Found: C, 49.40; H, 4.10; N, 12.16%. Calc. for $C_{28}H_{26}HgN_6S$: C, 49.50; H, 3.86; N, 12.38%. IR (cm^{-1}): 1600 ν(C=N)dpt and ν_{as}(C(H)=N), 1434 ν(N=N), 688 ν(C-S). ^{1}H NMR ($CDCl_3$): 9.22 [br s, 1H, NH], 8.35 [s, 1H, CH=N], 6.80-8.00 [m, 18H, ArH], 3.07 [s, 6H, $N(CH_3)_2$] ppm.

*2.3.3.4. Synthesis of (4-((E)-(4-methoxybenzylidene)amino)phenyl)(((Z)-((E)-phenyldiazenyl)(2-phenyl-hydrazono)methyl)thio)mercury(II) (**11**)*

A similar synthetic procedure as for **8** was used, except that **2** was replaced by **5**, giving a dark-red compound. Yield: 79%. M.p.: 166-168 °C. Found: C, 48.89; H, 3.55; N, 10.30%. Calc. for $C_{27}H_{23}HgN_5OS$: C, 48.67; H, 3.48; N, 10.52%. IR (cm^{-1}): 1621 ν(C=N)dpt, 1603 ν_{as}(C(H)=N), 1434 ν(N=N), 689 ν(C-S). ^{1}H NMR ($CDCl_3$): 9.21 [br s, 1H, NH], 8.39 [s, 1H, CH=N], 6.80-8.00 [m, 18H, ArH], 3.88 [s, 3H, OCH_3] ppm.

*2.3.3.5. Synthesis of (((Z)-((E)-phenyldiazenyl)(2-phenylhydrazono)methyl)thio)(4-((E)-(pyridin-2-ylmethylene)-amino)phenyl)mercury(II) (**12**)*

A similar synthetic procedure as for **8** was used, except that **2** was replaced by **7**, giving a dark-red compound. Yield: 88%. M.p.: 66-68 °C. Found: C, 47.35; H, 3.15; N, 13.20%. Calc. for $C_{25}H_{20}HgN_6S$: C, 47.12; H, 3.17; N, 13.20%. IR (cm^{-1}): 1624 ν(C=N)dpt and ν_{as}(C(H)=N), 1435 ν(N=N) and ν(C=N)py, 688 ν(C-S), 1593, 1497 ν(C=N)py. ^{1}H NMR ($CDCl_3$): 9.22 [br s, 1H, NH], 8.72 [d, 1H, H-9], 8.64 [s, 1H, CH=N], 6.80-8.20 [m, 17H, ArH] ppm.

*2.3.4. Reaction of **7** with $HgCl_2$:*

*2.3.4.1. Synthesis of (2-{[4-(acetyloxymercuryl)phenyl]iminomethyl}pyridine-κ^2N,N')dichloromercury(II) (**13**)*

To a hot solution of **7** (0.40 g, 0.907 mmol) in methanol (10 mL) was added a solution of $HgCl_2$ (0.29 g, 1.068 mmol, slight excess) in methanol (2 mL) under stirring conditions which resulted in the immediate formation of a pale yellow precipitate. The stirring was continued for 4 h. The precipitate was filtered and washed with methanol (3 x 1mL), hexane (3 x 5 mL) and dried *in vacuo*. The product was insoluble in common organic solvents. Yield: 67% (0.43 g). M.p.: 184-186 °C. Found: C, 23.35; H, 1.15; N, 3.80%. Calc. for $C_{14}H_{12}Cl_2Hg_2N_2O_2$: C, 23.59; H, 1.70; N, 3.93%. IR (KBr cm^{-1}): 1625 ν_{as}(OCO) and ν_{as}(C(H)=N), 1589, 1483, 1440 ν(C=N)py. ^{1}H NMR (DMSO-d_6): 8.99 [s, 1H, CH=N], 8.89 [d, J = 5.0 Hz, 1H, H-9], 8.20 [m, 2H, H-11,12], 7.79 [t, 1H, H-10], 7.55 [d, J = 8.5 Hz, 2H, H-2,6], 7.49 [d, J = 8.5 Hz, 2H, H-3,5], 1.97 [s, 3H, CH_3CO_2] ppm.

*2.3.5. Reaction of **1** with KCl:*

*2.3.5.1. Synthesis of chloro-(4-aminophenyl)mercury(II) (**14**)*

To a clear solution of **1** (1.0 g, 2.843 mmol) in methanol (50 ml), DMSO (3.0 mL) was added and then the methanol was recovered back from the reaction mixture (to facilitate filtration) using a rotary evaporator. To this, an aqueous solution (3 mL) containing KCl (0.42 g. 5.633 mmol) was added drop-wise under stirring conditions whereupon a thick white precipitate was obtained immediately. The stirring was continued for 8 h at ambient temperature and filtered. The residue was thoroughly washed with water, then with a small amount of methanol, dried on steam bath and finally *in vacuo*. The dried residue was recrystallized from methanol which afforded an off-white crystalline product. Yield 79% (0.68 g). M.p. 190-192 °C (d). Found: C, 22.06; H, 1.88; N, 4.30%. Calc. for C_6H_6ClHgN: C, 21.96; H, 1.84; N, 4.27%. IR (KBr cm^{-1}): 1630, 1588, 1493, 1410, 1257, 1183, 1112, 811, 506. ^{1}H NMR ($CDCl_3$): 7.07 [d, J = 8.0 Hz, 2H, H-2,6], 6.71 [d, J = 8.0 Hz, 2H, H-3,5], 3.78 [br s, 2H, NH_2] ppm.

*2.3.6. Reaction of **14** with pyridine-2-carbaldehyde:*

*2.3.6.1. Synthesis of 2-[((4-chloromercuryl)phenyl)iminomethyl]pyridine (**15**)*

A solution of pyridine-2-carbaldehyde (0.16 g, 1.493 mmol) in methanol (2 mL) was added to a clear methanolic solution (65 mL) of **14** (0.5 g, 1.523 mmol) whereupon the solution turned yellow immediately. The reaction mixture was stirred at ambient temperature for 4 h, which resulted in the formation of a yellow precipitate. The precipitate was filtered and dried *in vacuo*. The dried residue was boiled with hexane (3 x 5 mL), filtered and dried *in vacuo*. The crude product was recrystallized from acetonitrile which afforded the pure product in 75% (0.50 g) yield. M.p. 200-202 °C. Found: C, 34.45; H, 2.34; N, 6.70%. Calc. for $C_{12}H_9ClHgN_2$: C, 34.54; H, 2.17; N, 6.71%. IR (KBr cm^{-1}): 1625 ν_{as}(C(H)=N), 1586, 1480, 1435 ν(C=N)py. ^{1}H NMR ($CDCl_3$): 8.74 [d, J = 5.0 Hz, 1H, H-9], 8.57 [s,

1H, CH=N], 8.19 [d, J = 8.0 Hz, 1H, H-12], 7.84 [t, 1H, H-11], 7.20-7.45 [m, 5H, rest of the protons] ppm.

*2.3.7. Reaction of **15** with MCl_2 (M = Hg or Cd) and subsequent crystallization with DMSO or DMF:*

*2.3.7.1. Synthesis of (2-{[4-(chloromercuryl)phenyl]iminomethyl}pyridine-κ^2N,N')dichloromercury(II) (**16**)*

A similar synthetic procedure as for **13** was used, except that **7** was replaced by **15**, giving a yellow compound. The product was found to be insoluble in common organic solvents. Yield 80%. M.p. 220-222 °C (d). Found: C, 21.03; H, 1.42; N, 4.07%. Calc. for $C_{12}H_9Cl_3Hg_2N_2$: C, 20.93; H, 1.32; N, 4.07%. IR (cm^{-1}): 1624 ν_{as}(C(H)=N), 1590, 1483, 1440 ν(C=N)py. ^{1}H NMR (DMSO-d_6): 9.04 [s, 1H, CH=N], 8.95 [d, J = 5.0 Hz, 1H, H-9], 8.25 [t, 1H, H-11], 8.17 [d, J = 8.0 Hz, 1H, H-12], 7.84 [t, 1H, H-10], 7.59 [d, J = 8.5 Hz, 2H, H-2,6], 7.52 [d, J = 8.5 Hz, 2H, H-3,5] ppm.

*2.3.7.2. Synthesis of (2-{[4-(chloromercuryl)phenyl]iminomethyl}pyridine-κ^2N,N')dichlorocadmium(II) (**17**)*

A similar synthetic procedure as for **16** was used, except that $HgCl_2$ was replaced by $CdCl_2$, giving a yellow compound. The product was found to be insoluble in common organic solvents. Yield 67%. M.p. 282-284 °C. Found: C, 24.10; H, 1.61; N, 4.50%. Calc. for $C_{12}H_9CdCl_3HgN_2$: C, 24.00; H, 1.51; N, 4.66%. IR (cm^{-1}): 1623 ν_{as}(C(H)=N), 1590, 1482, 1441 ν(C=N)py. ^{1}H NMR (DMSO-d_6): 8.94 [d, J = 5.0 Hz, 1H, H-9], 8.82 [s, 1H, CH=N], 8.22 [t, 1H, H-11], 8.05 [d, J = 8.0 Hz, 1H, H-12], 7.82 [t, 1H, H-10], 7.50-7.40 [m, 4H, H-2,3,5,6,] ppm.

*2.3.7.3. Synthesis of (2-{[4-(chloromercuryl)phenyl]iminomethyl}pyridine-κ^2N,N')dichloromercury(II) (dimethylsulfoxide-κO) (**18**)*

Attempted crystallization of **16** in a DMSO/acetonitrile (1:3, v/v) mixture afforded dark-yellow crystals of compound **18** (see crystal structure). M.p.: 186-188 °C. Found: C, 21.80; H, 2.01; N, 3.50%. Calc. for $C_{14}H_{15}Cl_3Hg_2N_2OS$: C, 21.91; H, 1.97; N, 3.65%. IR (KBr cm^{-1}): 1625 ν_{as}(C(H)=N), 1590, 1488, 1437 ν(C=N)py, 1012 ν(S=O). ^{1}H NMR (DMSO-d_6): 8.97 [s, 1H, CH=N], 8.91 [d, J = 5.0 Hz, 1H, H-9], 8.18 [m, 2H, H-11,12], 7.78 [m, 1H, H-10], 7.59 [d, J = 8.5 Hz, 2H, H-2,6], 7.48 [d, J = 8.5 Hz, 2H, H-3,5] ppm. *Note: The signal at 2.53 ppm could not be assigned due to the signals from coordinated DMSO overlapping with those of the DMSO-d_6 solvent. The coordination of DMSO was judged on the basis of IR and this was subsequently confirmed from microanalytical data.*

*2.3.7.4. Synthesis of (2-{[4-(chloromercuryl)phenyl]iminomethyl}pyridine-κ^2N,N')dichloromercury(II) (dimethylformamide-κO) (**19**)*

Attempted crystallization of **16** in a DMF/acetonitrile (1:3, v/v) mixture afforded dark-yellow crystals of compound **19** (see crystal structure). M.p. >250 °C. Found: C, 23.74; H, 2.22; N, 5.55%. Calc. for $C_{15}H_{16}Cl_3Hg_2N_3O$: C, 20.65; H, 2.12; N, 5.52%. IR (cm^{-1}): 1647 ν(C=O) and ν_{as}(C(H)=N), 1592, 1489, 1436 ν(C=N)py. ^{1}H NMR (DMSO-d_6): 9.08 [s, 1H, CH=N], 8.97 [d, J = 5.0 Hz, 1H, H-9], 8.27 [t, 1H, H-11], 8.17 [d, J = 8.0 Hz, 1H, H-12], 7.94 [s, 1H, formyl H of DMF], 7.87 [t, 1H, H-10], 7.60 [d, J = 8.5 Hz, 2H, H-2,6], 7.52 [d, J = 8.5 Hz, 2H, H-3,5], 2.87 and 2.72 [s, 6H, -$N(CH_3)_2$ of DMF] ppm.

*2.3.7.5. Synthesis of (2-{[4-(chloromercuryl)phenyl]iminomethyl}pyridine-κ^2N,N')dichlorocadmium(II) (dimethylformamide-κO) (**20**)*

Attempted crystallization of **17** in a DMF/acetonitrile (1:3, v/v) mixture afforded dark-yellow crystals of compound **20** (see crystal structure). M.p. >250 °C. Found: C, 26.88; H, 2.42; N, 6.24%. Calc. for $C_{15}H_{16}CdCl_3HgN_3O$: C, 26.74; H, 2.39; N, 6.24%.IR (cm^{-1}): 1651 ν(C=O) and ν_{as}(C(H)=N), 1592, 1490, 1437 ν(C=N)py. ^{1}H NMR (DMSO-d_6): 8.67 [d, J = 5.0 Hz, 1H, H-9], 8.57 [s, 1H, CH=N], 7.97 [t, 1H, H-11], 7.82 [d, J = 8.0 Hz, 1H, H-12], 7.70 [s, 1H, formyl H of DMF], 7.57 [t, 1H, H-10], 7.27 [d, J = 8.5 Hz, 2H, H-2,6], 7.22 [d, J = 8.5 Hz, 2H, H-3,5], 2.64 and 2.48 [s, 6H, -N(CH_3)$_2$ of DMF] ppm.

2.4. X-ray crystallography

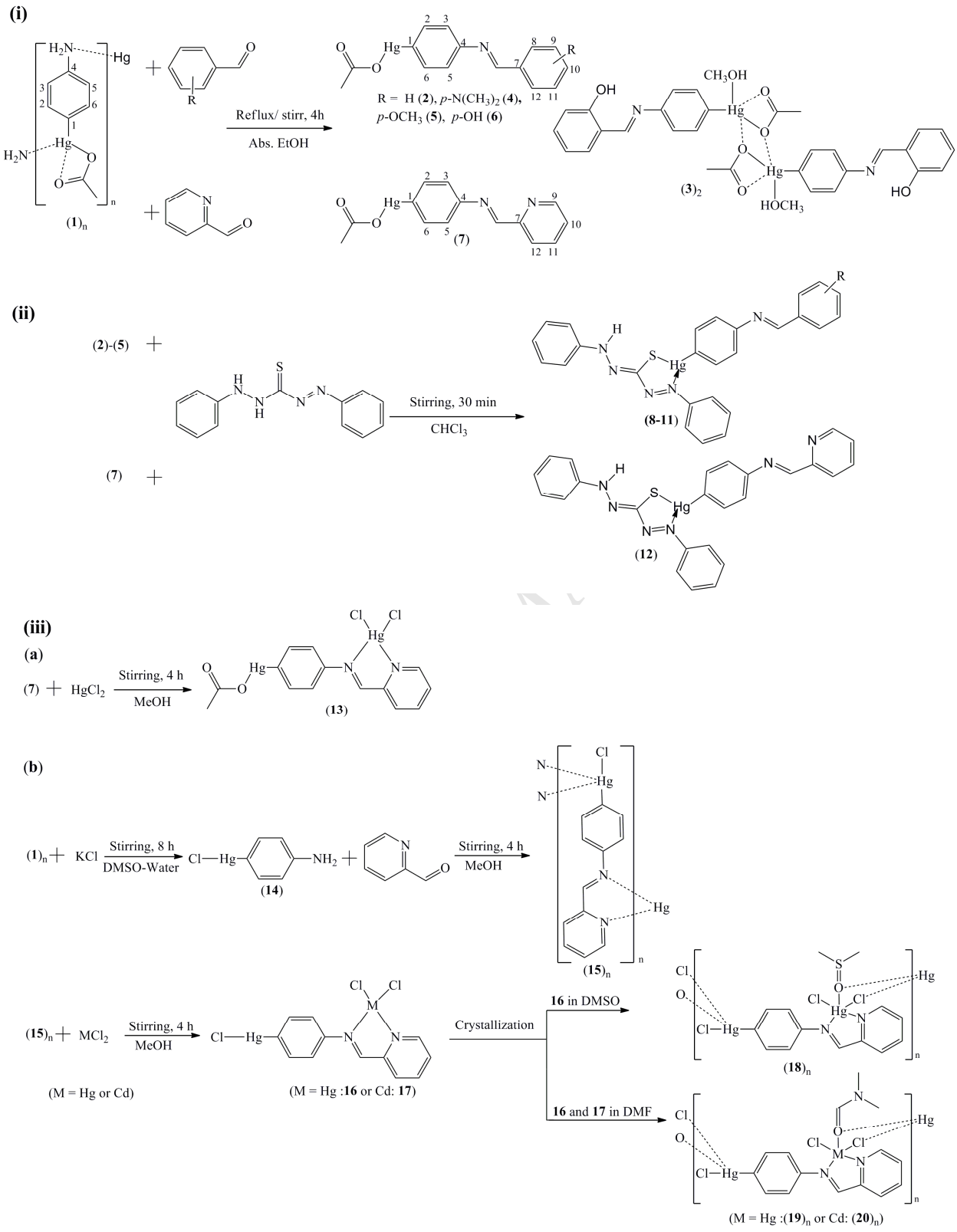
Crystals of compounds suitable for X-ray crystal-structure determination were obtained by slow evaporation of acetonitrile (**1** and **15**), acetonitrile/methanol (**3**), DMSO/acetonitrile (**18**), and DMF/acetonitrile (**19** and **20**) solutions of the respective compounds at room temperature. The measurements for **1**, **15, 18**, **19** and **20** were made at low temperature on an Agilent Technologies SuperNova area-detector diffractometer [42] using Mo Kα radiation (λ = 0.71073 Å) from a micro-focus X-ray source and an *Oxford Instruments Cryojet XL* cooler, while the data for **3** were recorded on a Nonius KappaCCD diffractometer [43] with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and an Oxford Cryosystems Cryostream 700 cooler. Data reduction was performed with CrysAlisPro [42] for **1**, **15**, **18**, **19** and **20** and using HKL Denzo and Scalepack [44] for **3**. The intensities were corrected for *Lorentz* and polarization effects. An empirical absorption correction based on the multi-scan method [45] was applied for **3**, an analytical absorption correction [46] was applied for **1**, **15, 18** and **19**, while a numerical absorption correction [47] was applied for **20**.

Equivalent reflections were merged. The data collection and refinement parameters are given in Table 1. The structures were solved by direct methods using *SHELXS97* [48], which revealed the positions of all non-hydrogen atoms. The non-hydrogen atoms were refined anisotropically. The amine H-atoms in **1** and the hydroxy H-atoms in **3** were placed in the positions indicated by a difference electron density map and their positions were allowed to refine together with individual isotropic displacement parameters. All remaining H-atoms were placed in geometrically calculated positions and refined by using a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to $1.2U_{eq}$ of its parent atom ($1.5U_{eq}$ for the methyl groups for all the compounds and hydroxy H-atom of the methanol solvent molecule in **3**). The refinement of each structure was carried out on F^2 by using full-matrix least-squares procedures, which minimized the function $\Sigma w(F_O^2 - F_C^2)^2$. A correction for secondary extinction was applied for **1** and **3**. One reflection in **3**, whose intensity was considered to be an extreme outlier, was omitted from the final refinement. The *SHELXL97* program [48] was used for all calculations. All crystallographic figures were drawn using *ORTEP-II* [49].

3. Results and discussion

3.1. Synthetic strategy

We began our investigation with the precursor acetyloxy(4-aminophenyl)mercury (**1**), which is an activator for enzymes (enzyme ligand), and moreover the structure of the product in solution can easily be identified by ^{1}H and ^{13}C NMR spectroscopy [40]. The presence of an amine group in **1** strongly increases the reactivity of the aromatic ring, due to an electron-donating effect. These merits led to further evaluation of the molecular structure of **1** in the solid state (see X-ray discussion). The syntheses of the organomercury compounds are outlined in Scheme 1 (i-iii).


(i)
Reflux/ stirr, 4h
Abs. EtOH
R = H (2), p-N(CH3)2 (4), p-OCH3 (5), p-OH (6)
(1)n
(7)
(3)2
(ii)
(2)-(5)
(7)
Stirring, 30 min
CHCl3
(8-11)
(12)
(iii)
(a)
(7) + HgCl2
Stirring, 4 h
MeOH
(13)
(b)
(1)n + KCl
Stirring, 8 h
DMSO-Water
(14)
Stirring, 4 h
MeOH
(15)n
(15)n + MCl2
Stirring, 4 h
MeOH
(M = Hg or Cd)
(M = Hg :16 or Cd: 17)
Crystallization
16 in DMSO
16 and 17 in DMF
(18)n
(M = Hg :(19)n or Cd: (20)n)

Scheme 1. The synthesis of polymeric acetyloxy(4-aminophenyl)mercury (**1**)$_n$, the materials produced from the reactions thereof (**2**-**20**) and the resulting coordination dimer (**3**)$_2$, organomercurio-ligand (**15**)$_n$ and bimetallic compounds **18**, **19** and **20**.

The acetyloxy(4-(arylideneamino)phenyl)mercury(II) complexes (**2**-**7**) were prepared from **1** by using the appropriate arylaldehyde in absolute ethanol according to the usual condensation reaction (Scheme 1 (i)) and these, upon reaction with dptc in chloroform followed by aqueous ammonia treatment, gave (phenyldiazenyl)(2-phenylhydrazono)ethyl)thio)mercury(II) derivatives (**8**-**12**) (Scheme 1 (ii)) by following a related procedure [50]. Organomercury compound **7**, which contains imino- and pyridyl nitrogen atoms capable of coordinating to additional metal atoms was reacted with a slight excess of mercuric chloride to give (2-{[4-(acetyloxymercuryl)phenyl]iminomethyl}pyridine-κ^2N,N')dichloromercury(II) (**13**).

Compounds **2**-**12** are soluble in polar organic solvents, such as chloroform, dichloromethane, acetonitrile and methanol, scarcely soluble in benzene, and insoluble in diethyl ether, hexane and petroleum ether. On the other hand, compound **13** was found to be insoluble in common organic solvents but moderately soluble in solvents with pronounced donor properties, such as dimethyl sulphoxide (DMSO), dimethylformamide (DMF) and pyridine. In another endeavor, reaction of **1** with KCl in DMSO-methanol yielded a chloro- analogue of **1**, chloro-(4-aminophenyl)mercury (**14**), which, upon treatment with pyridine-2-carbaldehyde, afforded the organomercurio-complex, 2-[((4-chloromercuryl)phenyl)iminomethyl]pyridine (**15**) and its molecular structure has also been determined in the solid state (see X-ray discussion). Compound **15**, upon treatment with $HgCl_2$ and followed by crystallization in DMSO, yielded **18** (Scheme 1(iii(b)), the structure of which was subsequently confirmed by single-crystal X-ray crystallography. As a final point, when DMF was

used as a solvent for crystallization instead of DMSO, the bimetallic (2-{[4-(chloromercuryl)phenyl]iminomethyl}pyridine-κ^2N,N')dichloromercury(II) (dimethylformamide -κO) (**19**) was obtained, structure of which was established by X-ray crystallography. The synthetic route to **19** was adopted for obtaining the heterobimetallic compound **20** using $CdCl_2$ in place of $HgCl_2$. Compounds **1**-**20** are all air stable and behave as non-electrolytes in acetonitrile solution.

3.2. Infrared, NMR spectra and photophysical properties

Some characteristic IR peaks of the compounds have been presented in the experimental section. The parent compound **1** displays a moderately intense band at 1628 cm^{-1} due to ν_{as}(OCO). In **2** and **5**, the bands at around 1620 cm^{-1} and 1603 cm^{-1} is assigned due to ν_{as}(OCO) and ν_{asy}(C(H)=N), respectively [51]. In **3**, **4** and **6**, a strong band centered in the region 1620-1605 cm^{-1} was detected where possibly both ν_{as}(OCO) and ν_{asy}(C(H)=N) overlap. On the other hand, the IR spectrum of the free dptc ligand displays absorption bands at 3437, 1440 and 1064 cm^{-1} due to ν(N-H), ν(N=N) and ν(C=S), respectively. The ν(C=S) band is found to be absent in **8**-**12**, as expected, while new bands, such as ν(C=N) and ν(C-S), were observed in the region of 1603-1624 cm^{-1} and at 688 cm^{-1}, respectively. However, the presence of ν_{asy}(C(H)=N), which is also expected in the region of ν(C=N), cannot be ruled out. A medium intensity sharp band at 1440 cm^{-1} due to ν(N=N) in **8**-**12**, shifts to lower frequency and appears at 1435 cm^{-1} as weak band upon complexation to mercury [52]. In addition to these, compound **12** exhibited bands of various intensity at 1593, 1497 and 1435 cm^{-1} (possibly merged with ν(N=N)), which are assigned to vibrations of the pyridine ring[51,53,54]. Thus, IR spectroscopic data suggest that the mercury atom is coordinated through the azo nitrogen atom and sulphur atom in the thiolic form of dptc. On the other hand, a very strong broad band in the region 1623 to 1565 cm^{-1} was observed in compound **7**, which is a consequence of

the overlap of bands from ν_{as}(OCO), ν_{as}(C(H)=N) and ν(C=N) of the pyridine ring [51,53,54], as expected. This broad band from **7** split into 1625 and 1589 cm^{-1} in compound **13**, where the former signal is due to overlap of both ν_{as}(OCO) and ν_{as}(C(H)=N), and the later is due to ν(C=N) of the pyridine ring. The presence of acetyloxy- and imino- protons in **13** was further confirmed from the ^{1}H NMR chemical shifts of the singlets at 1.97 and 8.99 ppm, respectively. In contrast, the ^{1}H NMR spectrum of compound **18** in DMSO-d_6 indicated the absence of acetate methyl protons, although the signal from the coordinated DMSO could not be detected owing to possible overlap with the residual solvent signal. In general, the IR spectrum of the crystalline compound **18** (in KBr) is very similar to that of **13**, except that a medium intensity band at 1012 cm^{-1} for **13** develops into a very strong band for **18**, which can safely be attributed to ν(S=O) of DMSO coordination to the mercury atom. This value is more than 40 cm^{-1} lower than that reported for free DMSO (1055 cm^{-1}) and is thus indicative of terminal (end-on) O-monocoordination. It should be noted that for S-bonded DMSO an increase of the frequency is to be expected [55,56]. This postulation was subsequently confirmed from the single-crystal structure of **18** (see X-ray discussion). The CO stretching vibration of free DMF at 1678 cm^{-1} shifts to a lower frequency at around 1650 cm^{-1} (ν Δ(CO) = ~ 30 cm^{-1}) in compounds **19** and **20**, which has been ascribed to the coordination of the oxygen atom of DMF to mercury [57,58]. The ^{1}H NMR data also support this mode of coordination. The ^{1}H NMR spectra of compounds **19** and **20** show two separate singlets for each methyl group (*cis* and *trans* to the carbonyl oxygen atom), which have been shifted up-field, indicating coordination of the oxygen atom of the DMF to the mercury atom. If the nitrogen atom was involved in coordination, the methyl groups would become equivalent and consequently only one NMR signal would be observed because of the loss of carbon-nitrogen double-bond character. In **19** and **20**, the band due to ν_{as}(C(H)=N) of DMF possibly overlaps with that of ν(C=O) of DMF, while those due to ν(C=N) of the pyridine ring were observed

in their expected positions. Lastly, the structures of **18** and **20** were confirmed by single-crystal structure analyses and correlate well with those expected from the spectroscopic data. The ^{1}H NMR spectra revealed the presence of the ligand skeleton in the respective compounds. The spectra of the compounds displayed expected signals, which correlate well with the hydrogen atoms present in the molecules. The resonance for the azomethine proton in the homobimetallic compounds (**16, 18** and **19**) appeared at around 9.0 ppm followed by a signal at around 8.95 ppm due to H-9, while a reverse trend was noted for the heterobimetallic compounds (**17** and **20**).

Table 2 summarizes the absorption and fluorescent properties of the studied compounds in acetonitrile. Compounds **2-7** display a single absorption in the range 315-357 nm, which is recorded in the experimental section along with the ε_{max} values. On the other hand, compounds **8-12** require specific mention. The photochromic behavior (yellow $\leftrightarrow$ blue) of bis(1,5-diphenylthiocarbazonato-*N*,*S*)mercury(II) [59,60], RHg(II) (R = Me, Ph), compounds with 1,5-diphenylthiocarbazonates [8,9] and 4-(4'-n-alkoxybenzylideneimino)phenylmercury(II) 1,5-diphenylthiocarbazonates [61] has been reported. Furthermore, examination of solutions of dptc in sixteen different organic solvents (except acetonitrile) showed that they comprise equilibrium mixtures of thiol and thione forms, which are individually responsible for the characteristic strong visible absorption bands around 440 and 620 nm [62]. The visible absorption spectra of **8-12** in acetonitrile solution are depicted in Fig. 1a along with the spectrum of dptc. The complexes exhibit only one band at 470 nm (an additional band at 354 in **10**) in contrast to free dptc (606 and 441 nm), and the λ_{max} values can safely be assigned to the normal yellow form [61]. On the other hand, the homobimetallic mercury compounds **13** and **16** are isostructural and they exhibit bands at 322 and 315 nm. Similar λ_{max} values were noted for the DMSO (**18**) and DMF adducts (**19**). The heterobimetallic compound **17** and its DMF adduct **20** also displayed a single absorption band at 334 and 324 nm, respectively. The observation of the bands in

bimetallic compounds (**13**, **16-20**) is possibly a result of overlap of intramolecular charge transfer transitions ($\varepsilon \sim 10^4$) with a weak band due to MLCT transition from Hg(II) $\rightarrow \pi^*$ (ligand), as observed for cognate systems [62-64]. Fig. 1b summarizes the absorption spectra of bimetallic compounds.

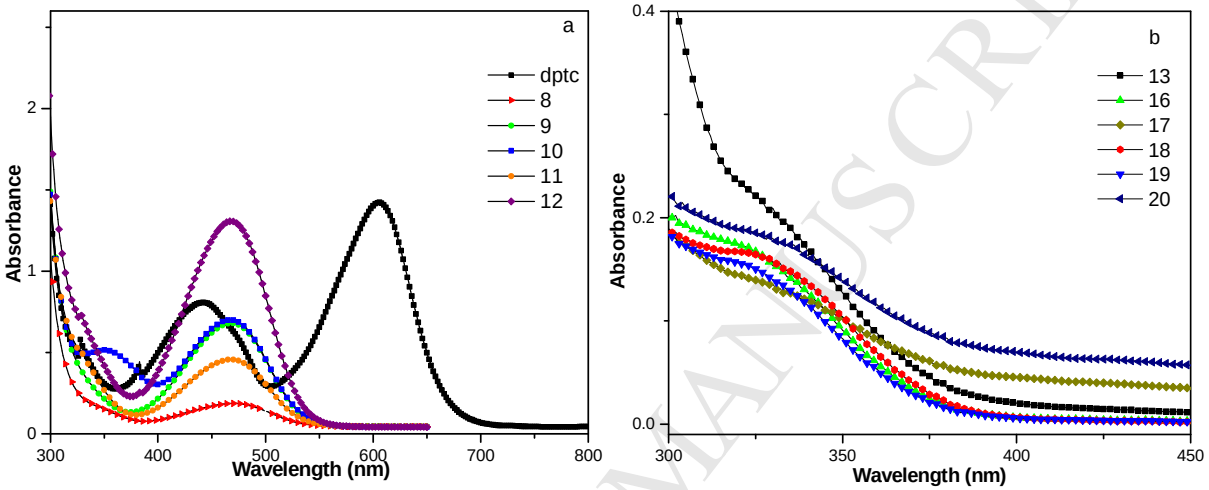


Fig. 1. Absorption spectra of (a) compounds **8-12** and 1,5-diphenylthiocarbazone (dptc) (concentration 10^{-5} M) and (b) bimetallic compounds **13-20** in acetonitrile (concentration 10^{-4} M)

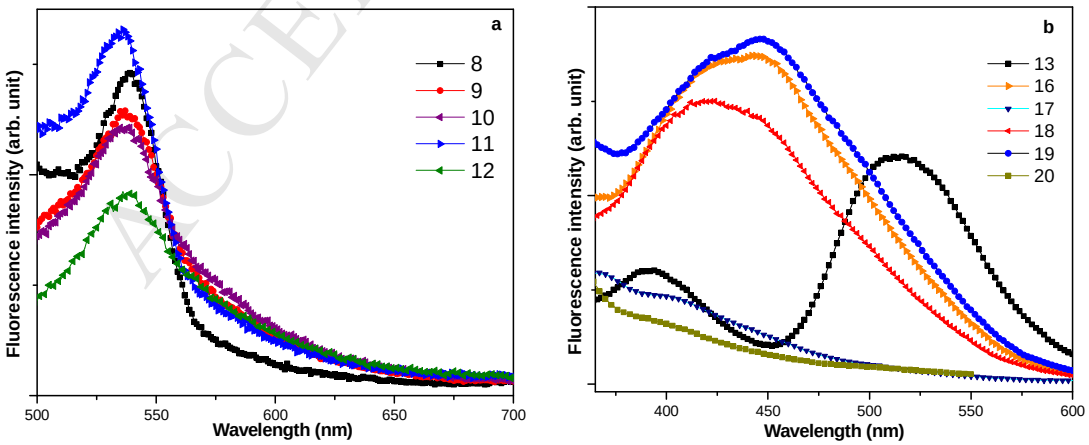


Fig.2.

Fig. 2. Fluorescence spectra of (a) compounds **8**-**12** and 1,5-diphenylthiocarbazone (dptc) (concentration ~10^{-5} M) and (b) compounds **13**, **16**-**20** (concentration ~10^{-4} M) in acetonitrile obtained by excitation at the respective absorption maxima (refer to Table 2).

Metals with the d^{10} configuration have attracted much attention recently due to their luminescent [64-67] and photochromic behavior [8,9,61] and it is from this perspective that the fluorescence properties of the compounds were investigated. In acetonitrile solution, compounds **8**-**12** (Fig. 2a) have broad emission bands at λ_{em} = 535 nm when they are excited at their respective absorption maxima (Fig. 1), with very low fluorescent quantum yield (ϕ_F). On the other hand, homobimetallic derivatives (**13**, **16**, **18** and **19**) (Fig. 2b), which also contain a α-diimine framework, show remarkably high fluorescent quantum yields (ϕ_F range from 0.65 to 0.89). The observed yields are four times higher in magnitude than those observed recently for mercury(II) compounds of (*E*)-*N*-(pyridin-2-ylmethylene)arylamines [64] and approximately seven times greater than those recorded for their organomercury ligand precursors **7** and **15**. The increase of ϕ_F can be attributed to the homobimetallic nature of the mercury atoms in the compounds. However, a decrease in ϕ_F was noted for the heterobimetallic compounds (**17** and **20**) where the metal atoms are different *i.e*. mercury-cadmium. Thus the ion selective behavior makes **15** a promising candidate as a metallo-ligand for the detection of mercury. Further work in this area is underway.

3.4. Description of the crystal structures

The crystal structures of some representatives of the synthesized compounds, $(\mathbf{1})_n$, $(\mathbf{3})_2$, $(\mathbf{15})_n$, $(\mathbf{18})_n$, $(\mathbf{19})_n$ and $(\mathbf{20})_n$, have been determined. The data collection and refinement parameters are

given in Table 1. The asymmetric unit of the parent acetyloxy(4-aminophenyl)mercury(II) compound, **1**, consists of one aniline ligand, one acetate ligand and a Hg-atom (Fig. 3(a)).

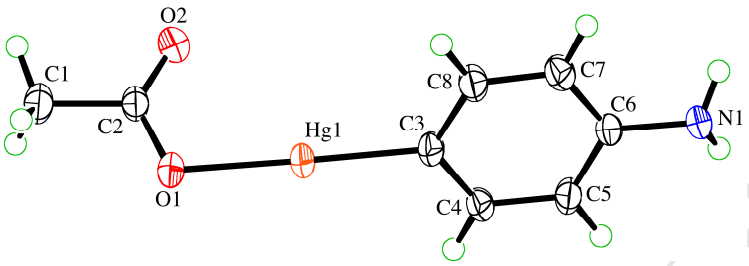


Fig. 3(a). The asymmetric unit of $(\mathbf{1})_n$. Displacement ellipsoids are shown at the 50% probability level.

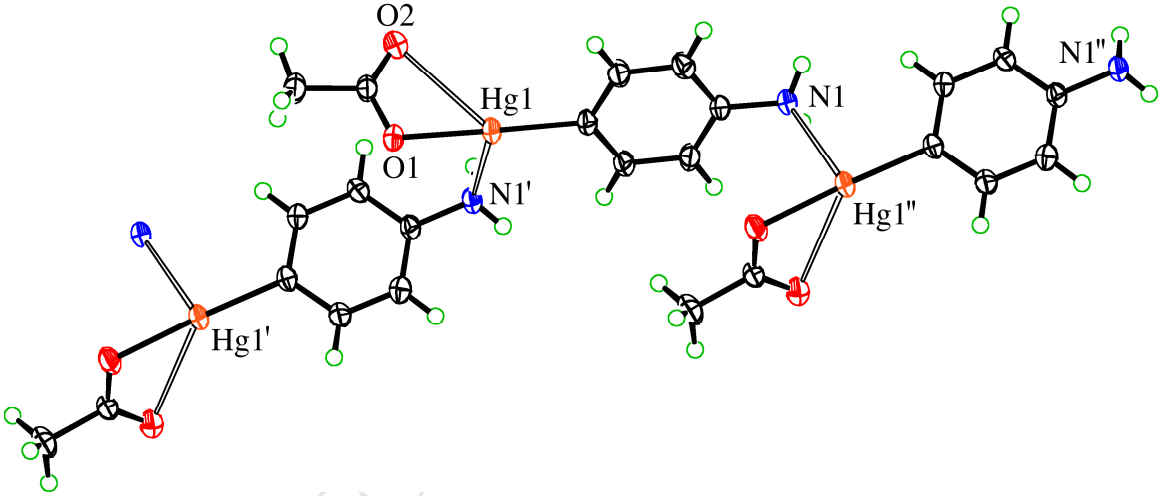


Fig. 3(b). Three repeats of the crystallographically and chemically unique unit in the polymeric chain structure of $(\mathbf{1})_n$ (50% probability ellipsoids; the symmetry codes for primed atoms are as in Table 3).

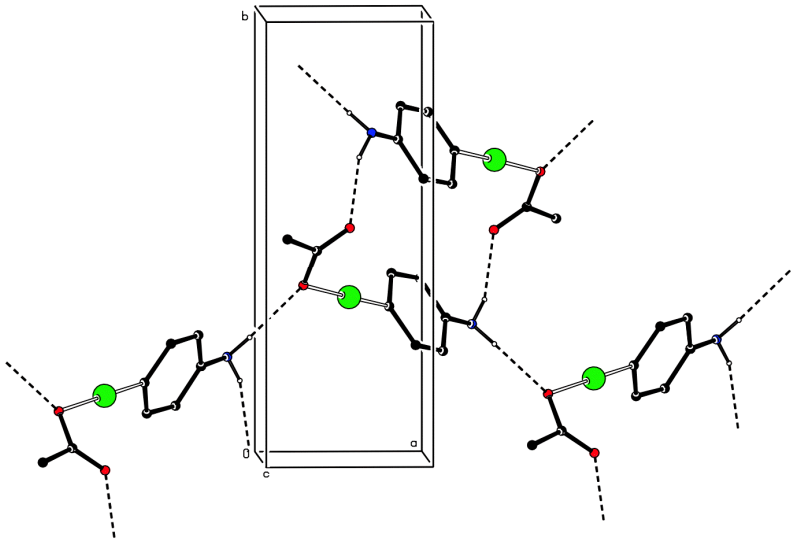


Fig. 3(c). Supramolecular aggregation leading to a two-dimensional hydrogen-bonded network in the crystal structure of (**1**)$_n$. Hydrogen bonding is shown as dashed lines.

The primary coordination sphere of the Hg-atom contains the *para* C-atom of the aniline ligand and an O-atom from the acetate ligand, disposed in a linear arrangement (C(3)–Hg(1)–O(1) = 174.64(18)°). The other O-atom of the acetate ligand has a long contact with the Hg-atom of 2.819(4) Å and the Hg-atom also has a long contact of 2.811(4) Å with the aniline N-atom from a neighboring molecule (Fig. 3(b)). These contacts are within the sum of the van der Waals radii [68, 69] of the involved atoms (ca. 3.3 Å, based on an estimate of 1.73 Å as the van der Waals radius of Hg [2,70], although this might be a considerable under bound [70]), so can be considered significant interactions although they do not seem to interfere significantly with the linear O–Hg–C geometry of the primary coordination sphere (Table 3). Related archetypal structures are those of (phenyl)mercury(II) acetate [71] and (*N*,*N*-dimethylaniline)mercury(II) acetate [72] in which the Hg–C distances are 1.92(6) and an average of 2.04(1) Å (two independent molecules), respectively, the Hg–O distances are 2.11(4) and 2.10(1) Å, the intramolecular Hg···O distances involving the other acetate O-atom are 2.85 and 2.83 Å and the C–Hg–O angles are 170(2) and 176.5(3)°,

respectively. With the exception of the somewhat short Hg–C bond in (phenyl)mercury(II) acetate, the geometries of these compounds are highly consistent with that of **1**. The propensity for arylamines to coordinate to a Hg-atom strongly via a C-atom and more weakly to an N-atom has been demonstrated in the crystal structures of bis[2-(pyridin-2'-yl)phenyl]mercury(II) [73] and (2-pyridylphenyl)mercury(II) chloride [74]; even though the Hg···N interaction is intramolecular in these examples, the Hg–C and Hg···N distances (2.07-2.10 and 2.63-2.80 Å, respectively) are also quite similar to those found in **1**.

Taking the long contacts into consideration, the units of compound **1** are linked into extended chains, which run parallel to the [10-1] direction. In this arrangement the Hg-atom is coordinated in a distorted trigonal pyramidal arrangement where the two O-atoms and the C-atom form a planar base around the Hg-atom and the long contact to the N-atom from the next unit in the chain occupies the apical position (Fig. 3(b)). The acetate O-atoms are not involved in any intermolecular Hg···O interactions up to at least 3.6 Å. In contrast, the structure of (phenyl)mercury(II) acetate [71] exhibits an intramolecular Hg···O contact of 2.85 Å and three intermolecular Hg···O contacts in the range 2.94-3.11 Å, while in the structure of (*N*,*N*-dimethylaniline)mercury(II) acetate [72] clusters of four molecules are formed by eight intermolecular Hg···O contacts in the range 2.7-2.8 Å; no Hg···N contacts of less than 3.6 Å are observed.

The amine group in **1** forms intermolecular hydrogen bonds with an acetate O-atom from each of two different neighboring chains (Table S1). One of the interactions links pairs of molecules related by a centre of inversion to form a loop motif with a graph set [75] of $R_2^2(20)$. The other interaction links the molecules into extended chains running in the [30-1] direction and exhibiting a graph set motif of C(8). Together, these interactions generate a two-dimensional hydrogen-bonding network

which lies parallel to the (103) plane (Fig. 3(c)). Within the two-dimensional network, a further C_2^2 (6) chain motif involving acetate groups alternating with $–NH_2$ groups is clearly evident. When the hydrogen-bonding interactions are combined with the chains formed by the Hg-coordination environment, the resulting supramolecular network is three-dimensional (Fig. S1).

The structure of (**3**)$_2$ (Fig. 4a, Table 4) is a centrosymmetric dimer with a Hg_2O_2 core. The asymmetric unit contains one imine, one acetate and one methanol ligand, plus one Hg-atom. The primary coordination sphere of the Hg-atom contains the *para* C-atom of the phenyl ring of the imine ligand and the carboxyl O-atom from the acetate ligand, disposed in a linear arrangement (C(3)–Hg(1)–O(1) = 177.7(2)°), plus longer contacts of 2.767(5) with the methanol ligand O-atom and 2.782(4) Å with the bridging carboxyl O-atom from the acetate ligand of the second component of the dimer. The two Hg-atoms in the dimer are thus asymmetrically doubly-bridged by the carboxyl O atoms from two acetate ligands. The Hg_2O_2 core is planar with the methanol ligands disposed perpendicular to this plane. The carbonyl O-atom of the acetate ligand has a long contact with its parent Hg-atom of 2.942(4) Å. The carbonyl O-atom also accepts a hydrogen bond from the hydroxy group of one of the methanol ligands of an adjacent dimer and is also 3.081(4) Å from the Hg-atom of that dimer to which the donor methanol ligand is not coordinated. These additional interactions serve to link the dimers into two-dimensional sheets which lie parallel to the (100) plane (Fig. 4(b)). The cores of the sheets contain the Hg and O-atoms, while the hydrophobic parts of the imine ligands extend perpendicular to the plane and interdigitate with the imine ligands of adjacent sheets. The main hydrogen-bond graph set motifs that can be discerned within the sheets are $C_2^2(12)$, C(4), C(6), and $R_4^4(20)$. The hydroxyphenyl group forms an intramolecular hydrogen bond with the

imine N-atom (Table S2) to give a ring with a graph set motif [75] of S(6). The imine ligands are not entirely planar, with the dihedral angle between the planes of the two phenyl rings being 15.0(3)°.

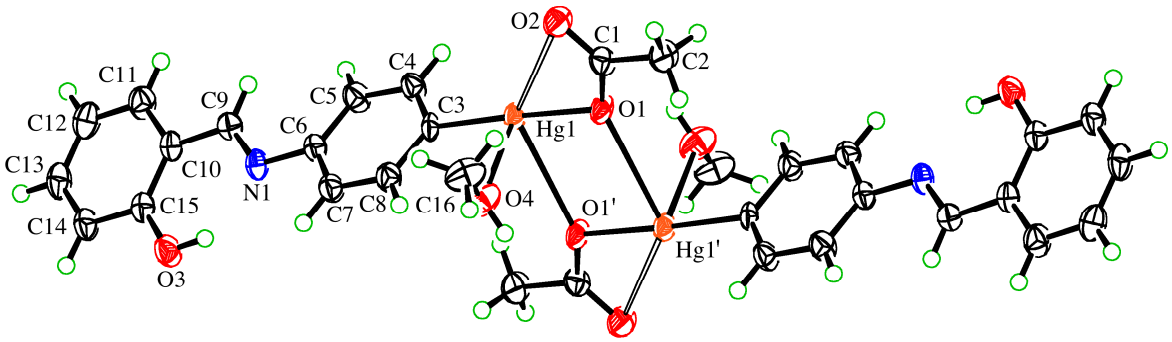


Fig. 4(a). The dimers found in the crystal structure of compound $(\mathbf{3})_2$ (50% probability ellipsoids; the symmetry codes for primed atoms are as in Table 4).

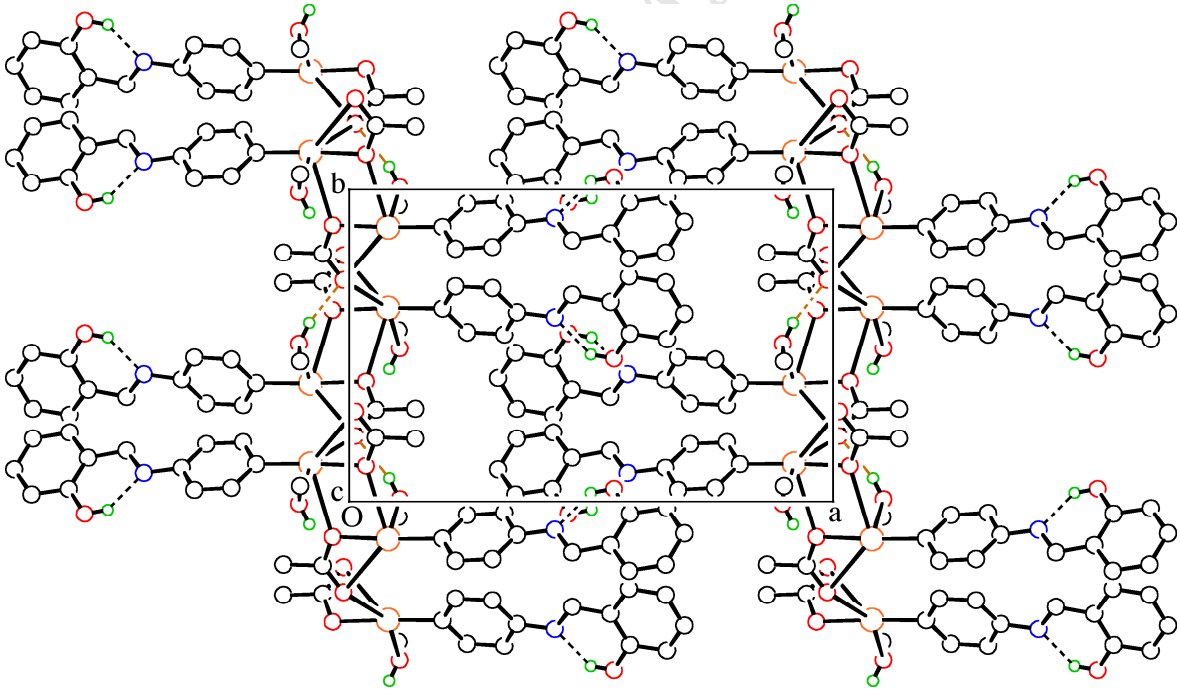


Fig. 4(b). The crystal packing of $(\mathbf{3})_2$ showing the two-dimensional layers resulting from the intermolecular hydrogen bonding (thin lines).

Compound **15** was synthesized as described earlier in order to replace the acetate ligand in **7** with a chloride ligand and provide the precursor for the construction of bimetallic mercuric chloride compounds **18** and **19,** and the cadmium chloride analogue; compound **20** (see Scheme 1). The crystal structures of these four compounds were determined. Compound **15** crystallizes as polymeric chains $(\mathbf{15})_n$ in which the asymmetric unit contains one imine and one chloride ligand, plus one Hg-atom. The primary coordination sphere of the Hg-atom contains the *para* C-atom of the phenyl ring of the imine ligand and the chloride ligand, disposed in a linear arrangement (C(10)–Hg(1)–Cl(1) = 167.40(6)°), which is complemented by two long Hg–N bonds (2.703(2) and 2.7017(19) Å) from both N-atoms of the imine ligand of an adjacent molecule (Fig. 5a, Table 5). This gives overall a see-saw coordination geometry about the Hg-atom. The imine ligand is thus moderately weakly bidentate in its coordination to one Hg-atom and bridges two Hg-atoms to give in the extended structure one-dimensional zig-zag chains, which run parallel to the [010] direction, as shown in Fig. 5(b). The imine ligands are distinctly non-planar, with the dihedral angle between the planes of the phenyl and pyridyl rings being 35.97(13)°. The chelating five-membered ring and the pyridine ring are, however, almost coplanar with a dihedral angle between their planes of 6.23(11)°.

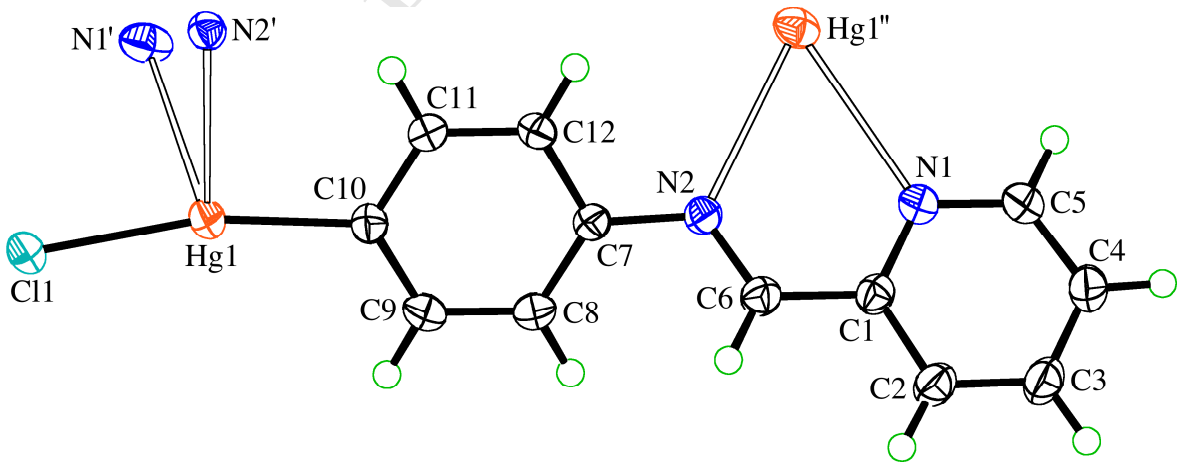


Fig. 5(a). The asymmetric unit of $(\mathbf{15})_n$ together with two long Hg–N bonds from the imine ligand of an adjacent molecule (50% probability ellipsoids; the symmetry codes for primed atoms are as in Table 5).

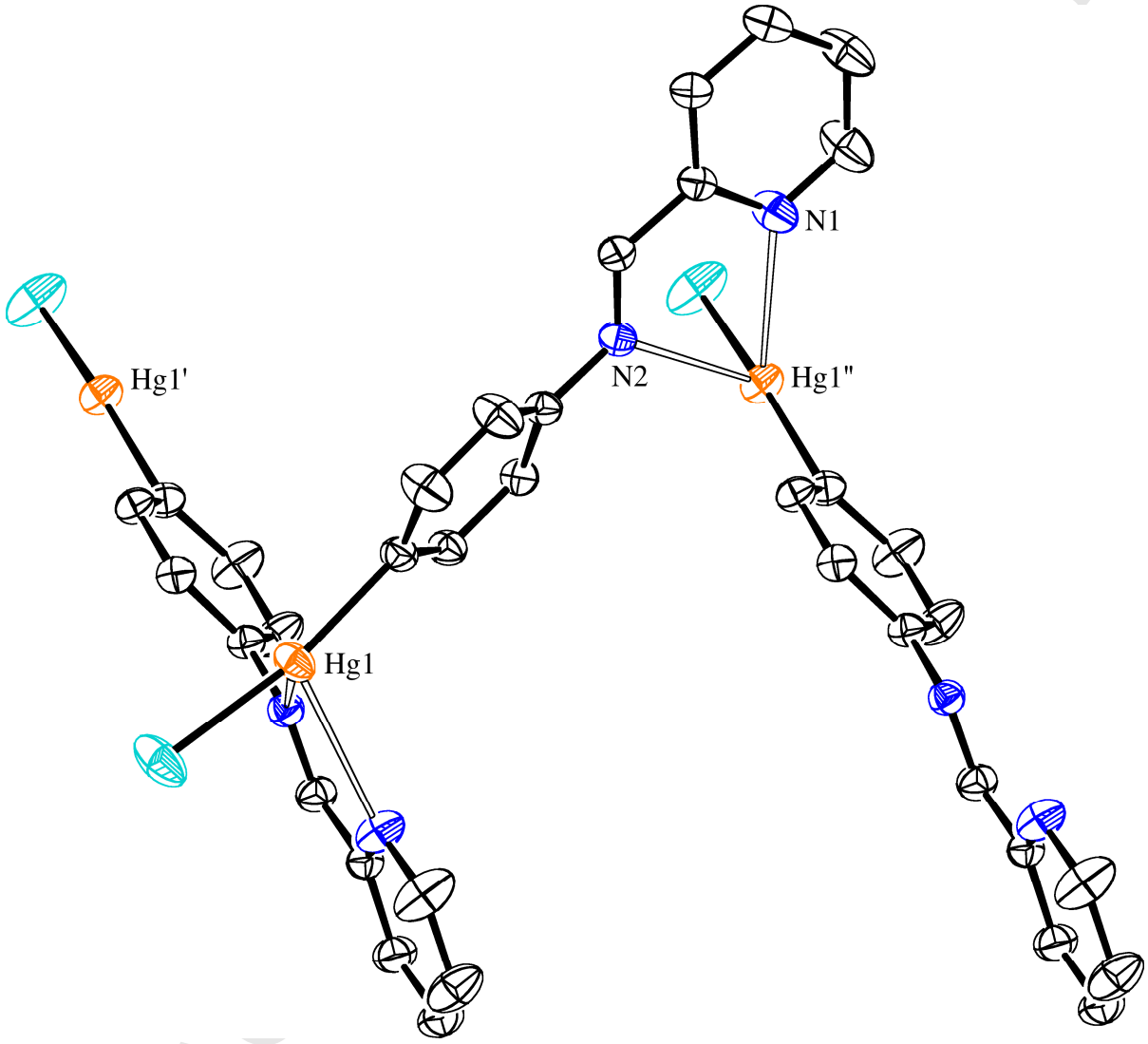


Fig. 5(b). Three repeats of the crystallographically and chemically unique unit in the zig-zag chain structure of $(\mathbf{15})_n$ (50% probability ellipsoids; the symmetry codes for primed atoms are as in Table 5).

When stirred with $HgCl_2$ in MeOH, the polymeric compound $(\mathbf{15})_n$ transformed into monomeric and dinuclear **16**, in which an additional $HgCl_2$ entity is bound to the imine ligand N-atoms. Subsequent crystallization from DMSO produced **18**, which has DMSO additionally coordinated to the Hg-atom of the $HgCl_2$ entity. The asymmetric unit of $(\mathbf{18})_n$ contains one imine, one DMSO and three chloride ligands, plus two symmetry-independent Hg-atoms (Fig. 6(a)). As in **3** and $(\mathbf{15})_n$, the primary coordination sphere of atom Hg(2) contains the *para* C-atom of the phenyl ring of the imine ligand and the chloride ligand, disposed in a linear arrangement (C(10)–Hg(2)–Cl(3) = 170.03(16)°). The second Hg-atom, Hg(1), is coordinated by two chloride ligands, both N-atoms of the imine ligand and the O-atom of the DMSO ligand to give a distorted trigonal bipyramidal coordination geometry with the DMSO O-atom and the imine N-atom as the axial ligands (Table 6). The Hg–N bond lengths of 2.310(4) and 2.464(4) Å are considerably shorter than those seen in $(\mathbf{15})_n$, where they were linking adjacent units in the polymeric chain, and are similar to those reported in the literature for a comparable complex with the same ligand: (di-μ-chloro)-bis{chloro[2-(phenyliminomethyl)-pyridine-κ^2N,N']mercury(II)} (2.322(9) and 2.496(8) Å) [76]. The imine Hg–N distances are consistently longer than the pyridine Hg–N distances in both these complexes. The imine ligand in **18** is twisted slightly, with the dihedral angle between the planes of the phenyl and pyridyl rings being 11.5(3)°. The planes of the chelating five-membered ring and the pyridine ring have a dihedral angle of 4.2(3)°. The O-atom of the DMSO ligand and one of the Cl-atoms, Cl(1), form a very weak double-bridge between atom Hg(1) and atom Hg(2) from an adjacent molecule and thus loosely link the molecules of **18** into extended zig-zag chains, which run parallel to the [010] direction (Fig. 6(b)). The Hg(2)···O(1') and Hg(2)···Cl(1') distances of 3.018(5) and 3.2054(14) Å (see Table 6 for symmetry codes of primed atoms) are approximately 0.23 and 0.27 Å, respectively, shorter than the estimated sum of the van der Waals radii of the involved atoms (ca. 3.25 and 3.48 Å, respectively

[69]). These bridges give atom Hg(2) a distorted see-saw coordination geometry, similar to that seen in **15**.

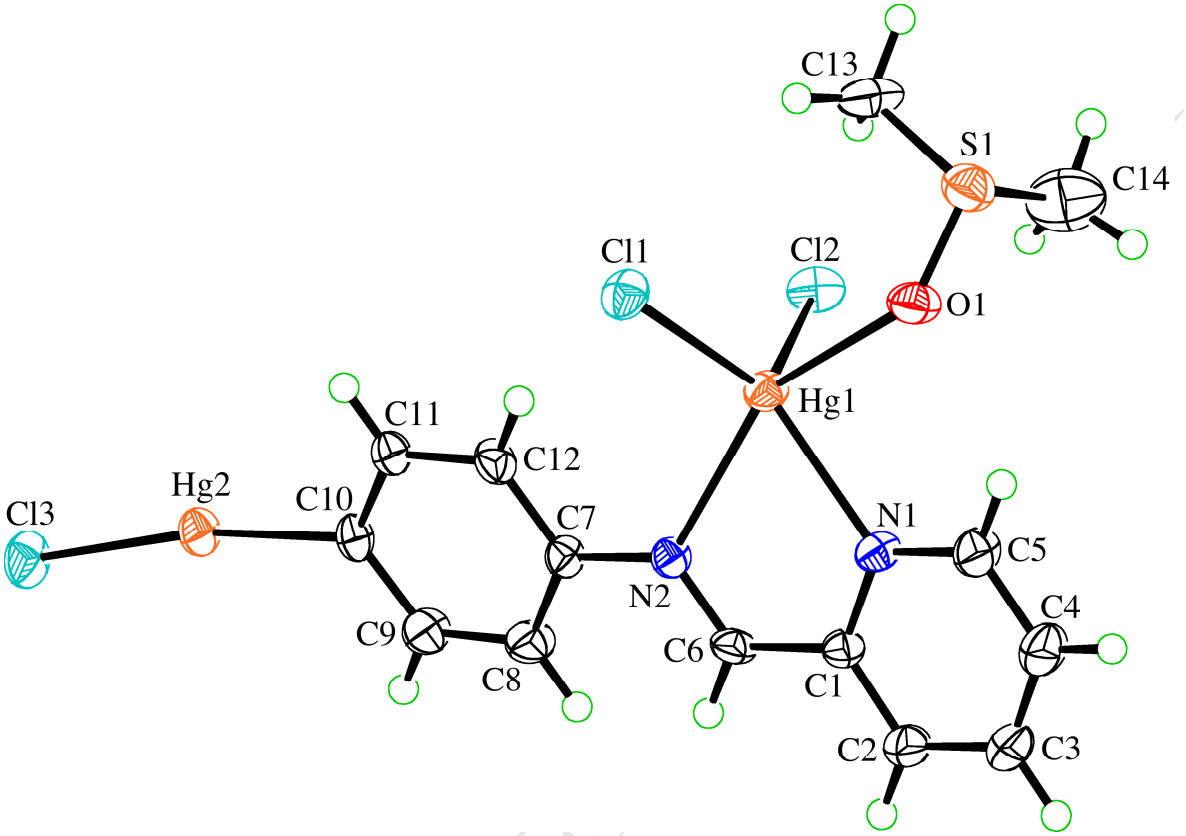


Fig. 6(a). The asymmetric unit of (**18**)$_n$ (50% probability ellipsoids).

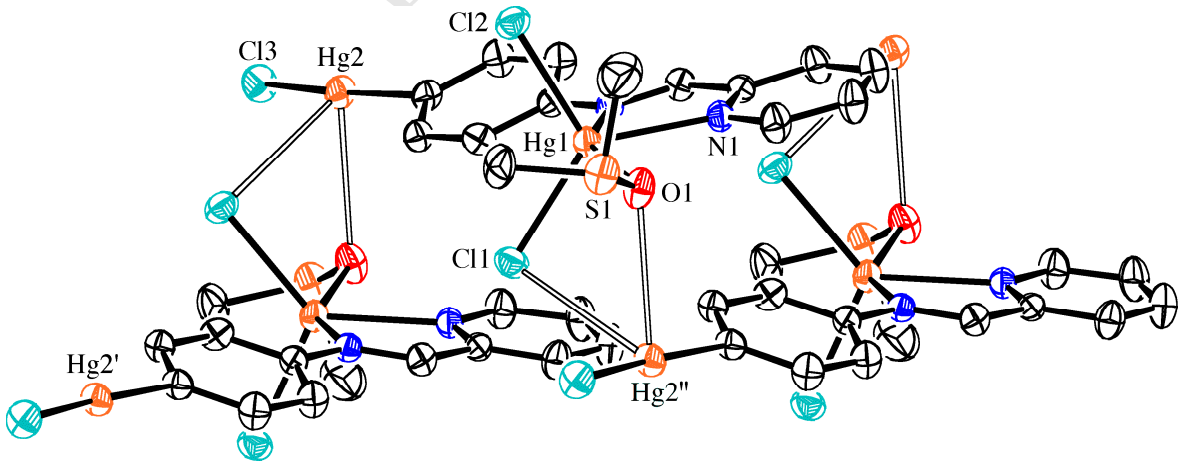


Fig. 6(b). Three repeats of the crystallographically and chemically unique unit in the zig-zag chain structure of $(\mathbf{18})_n$ showing the weak intermolecular Hg···Cl and Hg···Ocontacts as open bonds (50% probability ellipsoids; the symmetry codes for primed atoms are as in Table 6). The chain structures of $(\mathbf{19})_n$ and $(\mathbf{20})_n$ are similar.

When **16** was recrystallized from DMF, complex $(\mathbf{19})_n$ was obtained, which is essentially isomorphous with $(\mathbf{18})_n$, but DMF has replaced the DMSO ligand on the second Hg-atom (Fig. S2, Table 6). Reaction of **15** with $CdCl_2$ produced **17**, which has a Cd-atom coordinated to the imine ligand N-atoms instead of Hg, and recrystallisation from DMF gave $(\mathbf{20})_n$ (Fig. S3, Table 6), which is isostructural with $(\mathbf{19})_n$. In general, the differences between the Hg coordination geometries and the imine ligand geometries and conformations in $(\mathbf{18})_n$, $(\mathbf{19})_n$ and $(\mathbf{20})_n$ are almost negligible, although the trigonal bipyramidal coordination geometry around atom Hg(1) in $(\mathbf{18})_n$ is a little more distorted, particularly in the equatorial plane, which might be a consequence of the more compact DMSO ligand, which crowds closer to the Hg-atom than DMF does and thus has a greater steric influence.

The supramolecular architectures of $(\mathbf{19})_n$ and $(\mathbf{20})_n$ are the same as observed in $(\mathbf{18})_n$: the O-atom of the DMF ligand and one of the Cl-atoms from the MCl_2 unit (M = Hg, Cd) are positioned so to give the impression of a very weak double-bridge between the linearly coordinated Hg-atom and atom M from an adjacent molecule. As in $(\mathbf{18})_n$, these interactions link the molecules into extended zig-zag chains which run parallel to the [010] direction (Figs. S4 and S5). In $(\mathbf{19})_n$, the bridging Hg(2)···O(1') and Hg(2)···Cl(1') distances are 3.09(3) and 3.2342(8) Å, respectively, (see Table 6 for symmetry codes of primed atoms) which are ca. 0.16 Å and 0.25 Å shorter than the sum of the van der Waals radii of the involved atoms, so the contribution of the Hg···O interaction has

diminished compared with $(\mathbf{18})_n$. In $(\mathbf{20})_n$, the Hg(2)···O(1') and Hg(2)···Cl(1') distances are 3.304(2) and 3.1557(7) Å, respectively, the former now being 0.05 Å longer and the latter 0.32 Å shorter than the nominal sum of the van der Waals radii of the involved atoms. Thus, in $(\mathbf{20})_n$, the Hg···Cl interaction is clearly the dominant intermdecular interaction in the supramolecular aggregation.

4.0. Conclusion

In this work, we have described the isolation and characterization of some mono- and bi-metallic compounds (homobimetallics: organomercury/mercury; and heterobimetallics: (organomercury/cadmium), with designed imine-functionalized ligands, which were obtained from reactions with an enzyme activator i.e. acetyloxy(4-aminophenyl)mercury(II) (**1**). Efforts were made to determine the crystal and molecular structure of **1** owing to its important applications in biology. Reactions of **1** with arylaldehyde and 1,5-diphenylthiocarbazone (dptc) were thoroughly investigated and, indeed, the structure of a (*E*)-acetyloxy(4-((2-hydroxybenzylidene)amino)phenyl)mercury(II) compound in its dimeric form $(\mathbf{3})_2$ has been established. An organomercurio-ligand: 2-[((4-chloromercuryl)phenyl)iminomethyl]pyridine **15** was also prepared for the construction of bimetallic mercuric chloride compounds **18** and **19**, and cadmium chloride compound **20**. The compounds in the present investigation do not suffer much from solubility issues, which were alleviated by the use of appropriate functionalization of the organic groups. Additionally, the homobimetallic derivatives (**13**, **16**, **18** and **19**) displayed remarkably high fluorescent quantum yields, which are much higher in magnitude than those observed recently for mercury(II) compounds of (*E*)-*N*-(pyridin-2-ylmethylene)arylamines. Thus, the photoluminescent properties of these compounds may find applications in industry, despite the inherent toxicity of mercury. The preparation of compounds **19**

and **20** not only provides new insight into the reaction pathway, but also points to a new potential direction for the preparation of new organometal-metal mixed compounds. Related work in this area is under way.

Acknowledgments

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Appendix A. Supplementary data

CCDC 975005-975010 contain the supplementary crystallographic data for compounds **1**, **3**, **4** and **5**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix B. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/XXXX

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Table 1

Crystal data and refinement details for compounds $[\mathbf{1}]_n$, $[\mathbf{3}]_2$, $[\mathbf{15}]_n$, **18**, **19** and **20**

	$[\mathbf{1}]_n$	$[\mathbf{3}]_2$	$[\mathbf{15}]_n$	**18**	**19**	**20**
Empirical formula	$C_8H_9HgNO_2$	$C_{32}H_{34}Hg_2N_2O_8$	$C_{12}H_9ClHgN_2$	$C_{14}H_{15}Cl_3Hg_2N_2OS$	$C_{15}H_{16}Cl_3Hg_2N_3O$	$C_{15}H_{16}CdCl_3HgN_3O$
Formula weight	351.66	975.63	417.17	766.70	761.67	673.57
Crystal size (mm)	$0.20 \times 0.24 \times 0.26$	$0.13 \times 0.20 \times 0.28$	$0.15 \times 0.15 \times 0.17$	$0.05 \times 0.19 \times 0.24$	$0.07 \times 0.21 \times 0.21$	$0.07 \times 0.14 \times 0.19$
Crystal morphology	Prism	Tablet	Prism	Tablet	Tablet	Plate
Temperature (K)	160(1)	160(1)	160(1)	160(1)	160(1)	160(1)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	4.92005(11)	17.3643(3)	9.65338(10)	12.88146(18)	13.70236(14)	13.27198(12)
b (Å)	13.1192(3)	11.2320(2)	9.69517(11)	9.40234(13)	9.27138(8)	9.32523(8)
c (Å)	13.3172(3)	8.0080(1)	13.51274(14)	15.5583(3)	15.35088(18)	15.55275(15)
β (°)	93.5537(19)	90.5409(9)	104.0133(10)	97.8842(14)	101.8910(11)	101.6186(9)
V (Å^3)	857.93(3)	1561.78(4)	1227.04(2)	1866.55(5)	1908.32(3)	1891.91(3)
Z	4	2	4	4	4	4
D_x (g cm^{-3})	2.722	2.074	2.258	2.728	2.651	2.365
μ (mm^{-1})	17.935	9.893	12.761	17.010	16.533	9.679
Transmission factors (min, max)	0.027; 0.129	0.103; 0.333	0.177; 0.285	0.049, 0.277	0.092; 0.399	0.293; 0.630
θ range (°)	2.2-32.4	3.0-27.5	2.3-32.5	2.5-30.5	2.6-32.4	2.6-32.4
Reflections measured	13216	34822	19418	24551	30143	30657
Independent reflections; R_{int}	2904; 0.080	3577; 0.122	4118; 0.023	5161; 0.048	6425; 0.031	6376; 0.033
Reflections with $I > 2\sigma(I)$	2582	3263	3719	4412	5692	5669
Number of parameters	119	206	145	210	219	219
$R(F)$ [$I > 2\sigma(I)$ reflns]	0.0359	0.0406	0.0185	0.0302	0.0230	0.0233
$wR(F^2)$ (all data)	0.0960	0.1101	0.0429	0.0707	0.0506	0.0525
GOF(F^2)	1.076	1.067	1.073	1.070	1.068	1.043
$\Delta\rho_{max, min}$ (e, Å^{-3})	1.84, -1.80	3.88, -4.16	1.20, -1.23	2.21, -1.61	2.87; -1.45	1.68; -1.32

Table 2

Photophysical data for the studied compounds in acetonitrile solution

Compounds	Electronic spectroscopic data λ_{max} (nm); (ε[M^{-1} cm^{-1}])	Photoluminescence data λ_{em} (nm)	ϕ_F
dptc	606 (35,250), 441 (20,000)		
8	471 (4,500)	538	0.008
9	469 (16,750)	536	0.016
10	467 (17,250), 354 (12,807)	533	0.017
11	467 (11,250)	535	0.017
12	467 (32,250)	539	0.016
13	322 (2,162)	514, 391	0.895
16	315 (1,676)	441, 419 sh	0.845
17	334 (1,356)	507, 403 sh	0.336
18	319 (1,529)	443, 420 sh	0.653
19	319 (1,529)	443, 420 sh	0.653
20	323 (1,866)	510, 399 sh	0.169

Table 3

Selected bond lengths (Å) and angles (°) for $[\mathbf{1}]_n$[a]

Hg(1)-C(3)	2.035(5)	O(1)-Hg(1)-O(2)	51.11(13)
Hg(1)-O(1)	2.092(3)	C(3)-Hg(1)-N(1')	98.94(17)
Hg(1)-O(2)	2.819(4)	O(1)-Hg(1)-N(1')	86.09(15)
Hg(1)-N(1')	2.811(4)	O(2)-Hg(1)-N(1')	91.06(12)
		C(6)-N(1)-Hg(1")	112.4(3)
C(3)-Hg(1)-O(1)	174.64(18)	C(2)-O(1)-Hg(1)	108.6(3)
C(3)-Hg(1)-O(2)	130.12(17)	C(2)-O(2)-Hg(1)	76.1(3)

[a] Primed atoms refer to the molecule in the following symmetry related positions: ' -0.5+*x*, 0.5-*y*, 0.5+*z*; " 0.5+*x*, 0.5-*y*, -0.5+*z*.

Table 4

Selected bond lengths (Å) and angles (º) for $[\mathbf{3}]_2$[a]

Hg(1)-C(3)	2.048(6)	O(1)-Hg(1)-O(2)	48.7(1)
Hg(1)-O(1)	2.093(4)	C(3)-Hg(1)-O(2)	133.3(2)
Hg(1)-O(2)	2.942(4)	O(4)-Hg(1)-O(2)	88.1(1)
Hg(1)-O(4)	2.767(5)	O(1')-Hg(1)-O(2)	122.3(1)
Hg(1)-O(1')	2.782(4)	C(3)-Hg(1)-O(2'')	105.0(2)
Hg(1)-O(2'')	3.081(4)	O(1)-Hg(1)-O(2'')	76.0(2)
Hg(1)-C(3)	2.048(6)	O(4)-Hg(1)-O(2'')	155.7(1)
		O(1')-Hg(1)-O(2'')	92.7(1)
C(3)-Hg(1)-O(1)	177.7(2)	O(2)-Hg(1)-O(2'')	85.82(8)
C(3)-Hg(1)-O(4)	96.2(2)	C(2)-O(1)-Hg(1')	138.7(4)
O(1)-Hg(1)-O(4)	82.4(2)	Hg(1)-O(1)-Hg(1')	105.0(2)
C(3)-Hg(1)-O(1')	102.8(2)	C(2)-O(2)-Hg(1''')	135.4(4)
O(1)-Hg(1)-O(1')	75.0(2)	Hg(1)-O(2)-Hg(1''')	110.5(1)
O(4)-Hg(1)-O(1')	70.9(2)	C(2)-O(1)-Hg(1)	113.6(3)

[a] Primed atoms refer to the molecule in the following symmetry related positions: ' -*x*, 1-*y*, -*z*; '' *x*, 1.5-*y*, 0.5+*z*; ''' *x*, 1.5-*y*, -0.5+*z*.

Table 5

Selected bond lengths (Å) and angles (º) for $[\mathbf{15}]_n$[a]

Hg(1)-C(10)	2.058(2)	Cl(1)-Hg(1)-N(1')	86.24(6)
Hg(1)-Cl(1)	2.3447(7)	Cl(1)-Hg(1)-N(2')	95.63(4)
Hg(1)-N(1')	2.703(2)	N(2')-Hg(1)-N(1')	61.62(6)
Hg(1)-N(2')	2.7017(19)	C(5)-N(1)-Hg(1'')	123.53(18)
		C(1)-N(1)-Hg(1'')	118.51(16)
C(10)-Hg(1)-Cl(1)	167.40(6)	C(6)-N(2)-Hg(1'')	119.19(15)
C(10)-Hg(1)-N(2')	93.96(8)	C(7)-N(2)-Hg(1'')	120.38(13)
C(10)-Hg(1)-N(1')	105.54(8)		

[a] Primed atoms refer to the molecule in the following symmetry related positions: ' 0.5-*x*, 0.5+*y*, 0.5-*z*; '' 0.5-*x*, -0.5+*y*, 0.5-*z*.

Table 6

Selected bond lengths (Å) and angles (º) for **18**, **19** and **20**[a]

	18	**19**	**20**
M(1)-N(1)	2.310(4)	2.296(3)	2.319(2)
M(1)-N(2)	2.464(4)	2.505(3)	2.417(2)
M(1)-Cl(1)	2.4679(14)	2.4283(8)	2.4426(6)
M(1)-Cl(2)	2.4172(14)	2.4629(8)	2.4544(7)
M(1)-O(1)	2.580(4)	2.592(3)	2.342(2)
Hg(2)-C(10)	2.057(5)	2.062(3)	2.057(3)
Hg(2)-Cl(3)	2.3275(13)	2.3267(9)	2.3282(7)
Hg(2)···O(1')	3.018(5)	3.091(3)	3.304(2)
Hg(2)···Cl(1')	3.2054(14)	3.2342(8)	3.1557(7)
N(1)-M(1)-Cl(1)	112.42(12)	134.11(7)	132.32(6)
N(1)-M(1)-Cl(2)	132.92(12)	116.44(7)	117.22(6)
N(2)-M(1)-Cl(1)	97.77(11)	105.46(6)	104.08(5)
N(2)-M(1)-Cl(2)	107.24(11)	105.90(6)	101.10(5)
N(1)-M(1)-N(2)	70.82(15)	70.87(9)	71.64(8)
Cl(1)-M(1)-Cl(2)	114.37(5)	108.60(3)	110.25(2)
N(1)-M(1)-O(1)	81.73(14)	80.89(9)	81.38(8)
N(2)-M(1)-O(1)	151.24(13)	151.03(9)	152.80(7)
Cl(1)-M(1)-O(1)	100.52(10)	89.39(7)	91.35(6)
Cl(2)-M(1)-O(1)	85.08(11)	92.16(7)	94.14(6)
C(10)-Hg(2)-Cl(3)	170.03(16)	172.84(10)	171.16(8)
C(1)-N(1)-M(1)	116.9(3)	116.9(2)	115.30(17)
C(5)-N(1)-M(1)	124.1(4)	124.5(2)	126.5(2)
C(6)-N(2)-M(1)	111.8(3)	111.0(2)	112.58(18)
C(7)-N(2)-M(1)	126.2(3)	128.69(19)	127.85(16)
X-O(1)-M(1)	127.2(2)	118.4(2)	122.8(2)
X-O(1)···Hg(2")	115.0(2)	134.8(3)	133.39(19)
M(1)-O(1)···Hg(2")	93.96(13)	92.29(8)	91.89(7)
M(1)-Cl(1)···Hg(2")	92.69(4)	92.03(3)	93.67(2)

[a] M = Hg for **18**, **19** and Cd for **20**; X = S(1) for **18** and C(13) for **19**, **20**. Primed atoms refer to the molecule in the following symmetry related positions for **18**: ' 1-*x*, 0.5+*y*, 1.5-*z*; " 1-*x*, -0.5+*y*, 1.5-*z*; and for **19**, **20**: ' 2-*x*, -0.5+*y*, 1.5-*z*; " 2-*x*, 0.5+*y*, 1.5-*z*.

Captions to the Scheme and Figures:

Scheme 1. The synthesis of polymeric acetyloxy(4-aminophenyl)mercury $(\mathbf{1})_n$, the materials produced from the reactions thereof (**2**-**20**) and the resulting coordination dimer $(\mathbf{3})_2$, organomercurio-ligand $(\mathbf{15})_n$ and bimetallic compounds **18**, **19** and **20**.

Fig. 1. Absorption spectra of (a) compounds **8**-**12** and 1,5-diphenylthiocarbazone (dptc) (concentration 10^{-5} M) and (b) bimetallic compounds **13**-**20** in acetonitrile (concentration 10^{-4}M).

Fig.2. Fluorescence spectra of (a) compounds **8**-**12** and 1,5-diphenylthiocarbazone (dptc) (concentration ~10^{-5} M) and (b) compounds **13**, **16**-**20** (concentration ~10^{-4} M) in acetonitrile obtained by excitation at the respective absorption maxima (refer to Table 2).

Fig. 3(a). The asymmetric unit of $(\mathbf{1})_n$. Displacement ellipsoids are shown at the 50% probability level.

Fig. 3(b). Three repeats of the crystallographically and chemically unique unit in the polymeric chain structure of $(\mathbf{1})_n$ (50% probability ellipsoids; the symmetry codes for primed atoms are as in Table 3).

Fig. 3(c). Supramolecular aggregation leading to a two-dimensional hydrogen-bonded network in the crystal structure of $(\mathbf{1})_n$. Hydrogen bonding is shown as dashed lines.

Fig. 4(a). The dimers found in the crystal structure of compound $(\mathbf{3})_2$ (50% probability ellipsoids; the symmetry codes for primed atoms are as in Table 4).

Fig. 4(b). The crystal packing of $(\mathbf{3})_2$ showing the two-dimensional layers resulting from the intermolecular hydrogen bonding (thin lines).

Fig. 5(a). The asymmetric unit of (**15**)$_n$ together with two long Hg–N bonds from the imine ligand of an adjacent molecule (50% probability ellipsoids; the symmetry codes for primed atoms are as in Table 5).

Fig. 5(b). Three repeats of the crystallographically and chemically unique unit in the zig-zag chain structure of (**15**)$_n$ (50% probability ellipsoids; the symmetry codes for primed atoms are as in Table 5).

Fig. 6(a). The asymmetric unit of (**18**)$_n$ (50% probability ellipsoids).

Fig. 6(b). Three repeats of the crystallographically and chemically unique unit in the zig-zag chain structure of (**18**)$_n$ showing the weak intermolecular Hg···Cl and Hg···Ocontacts as open bonds (50% probability ellipsoids; the symmetry codes for primed atoms are as in Table 6).

Highlights

► An organomercury enzyme activator: Compound **1**
► Metallo-*N*,*N'*-donor ligand: **15**
► Homo-bimetallic organomercury/mercury mixed compounds (**18**, **19**)
► Heterobimetallic organomercury/cadmium mixed compound (**20**)
►IR, NMR, Photophysical properties and structures

An organomercury enzyme activator as a versatile template for new organomercury(II) compounds encompassing homo-bimetallic (RHg/Hg) and hetero-bimetallic (RHg/Cd) compositions: Syntheses, photoluminescence and structures

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ELECTRONIC SUPPLEMENTARY INFORMATION

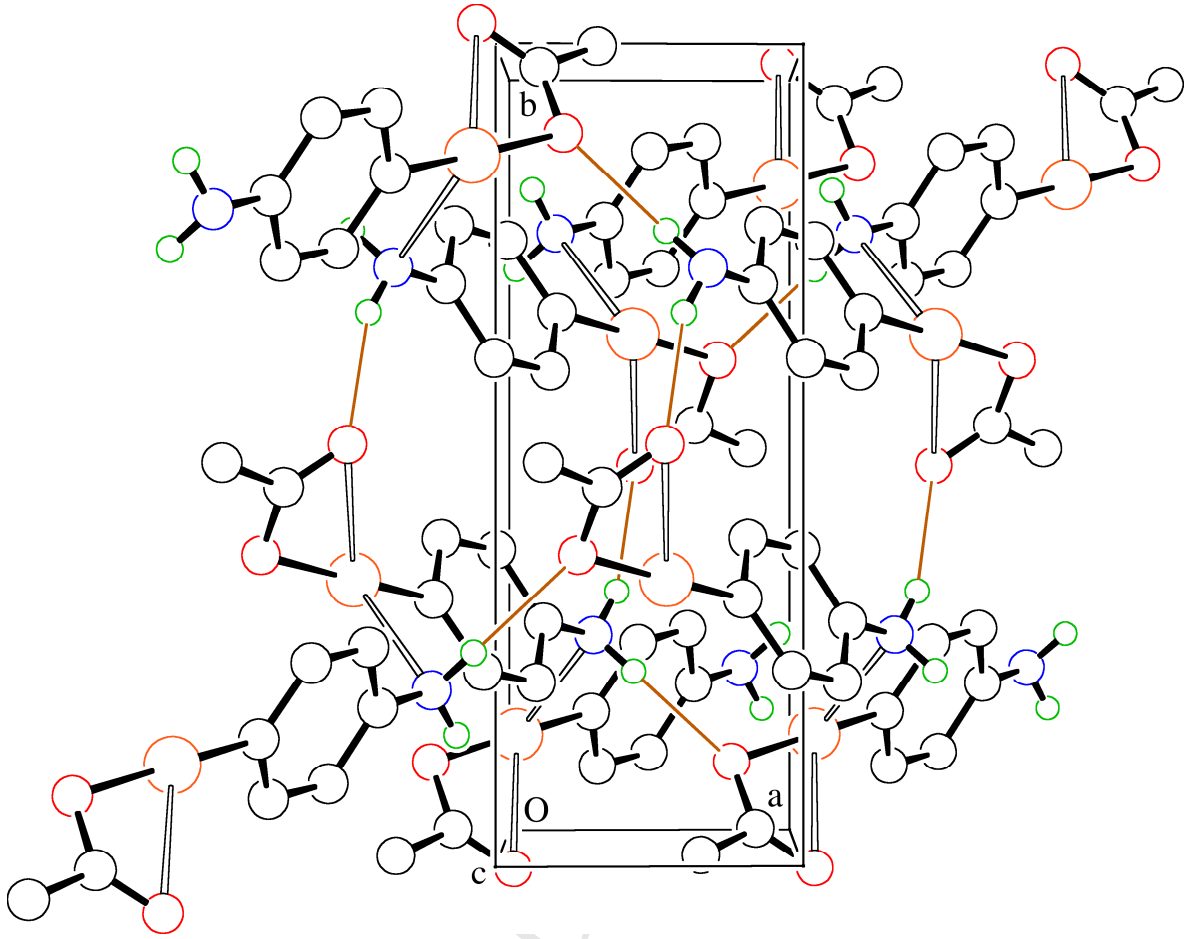

Fig. S1. The molecular packing of $(\mathbf{1})_n$ showing the intermolecular hydrogen bonding and the overall three-dimensional supramolecular framework.

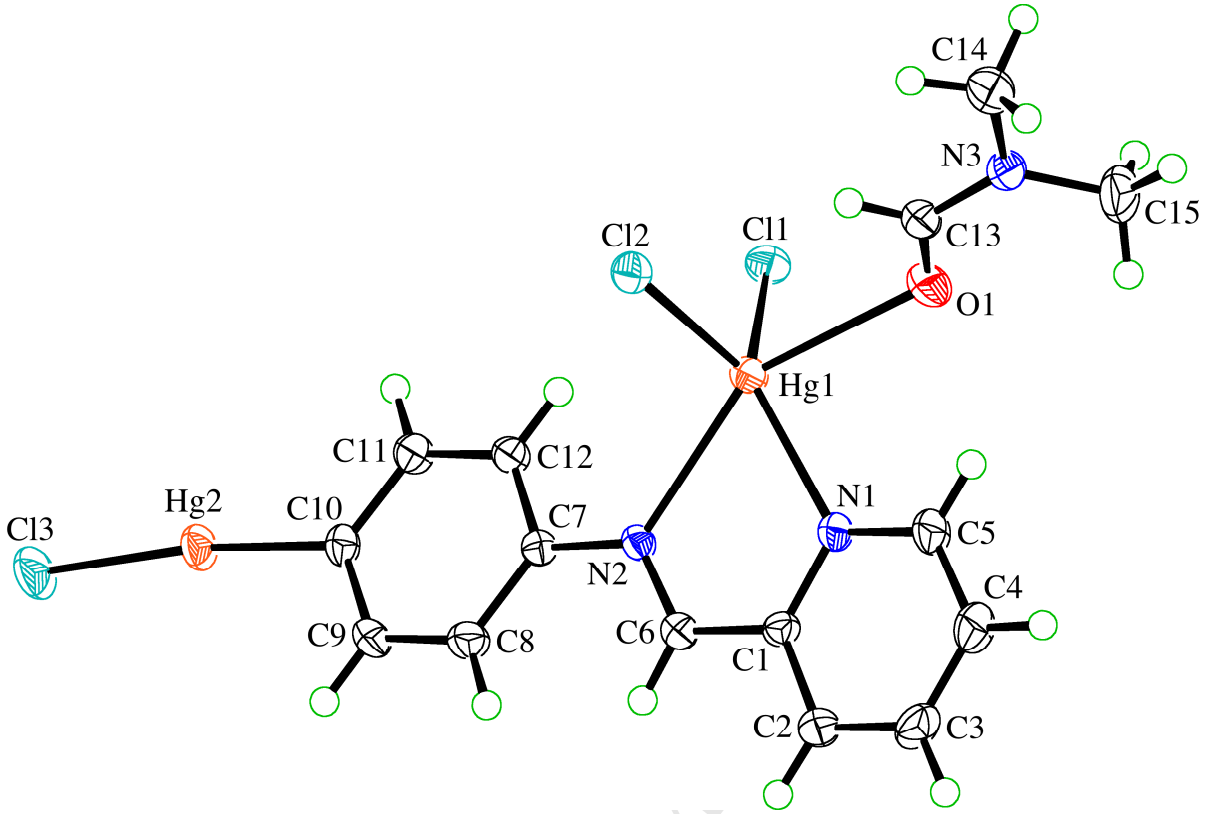

Fig. S2. The asymmetric unit of $(\mathbf{19})_n$ (50% probability ellipsoids).

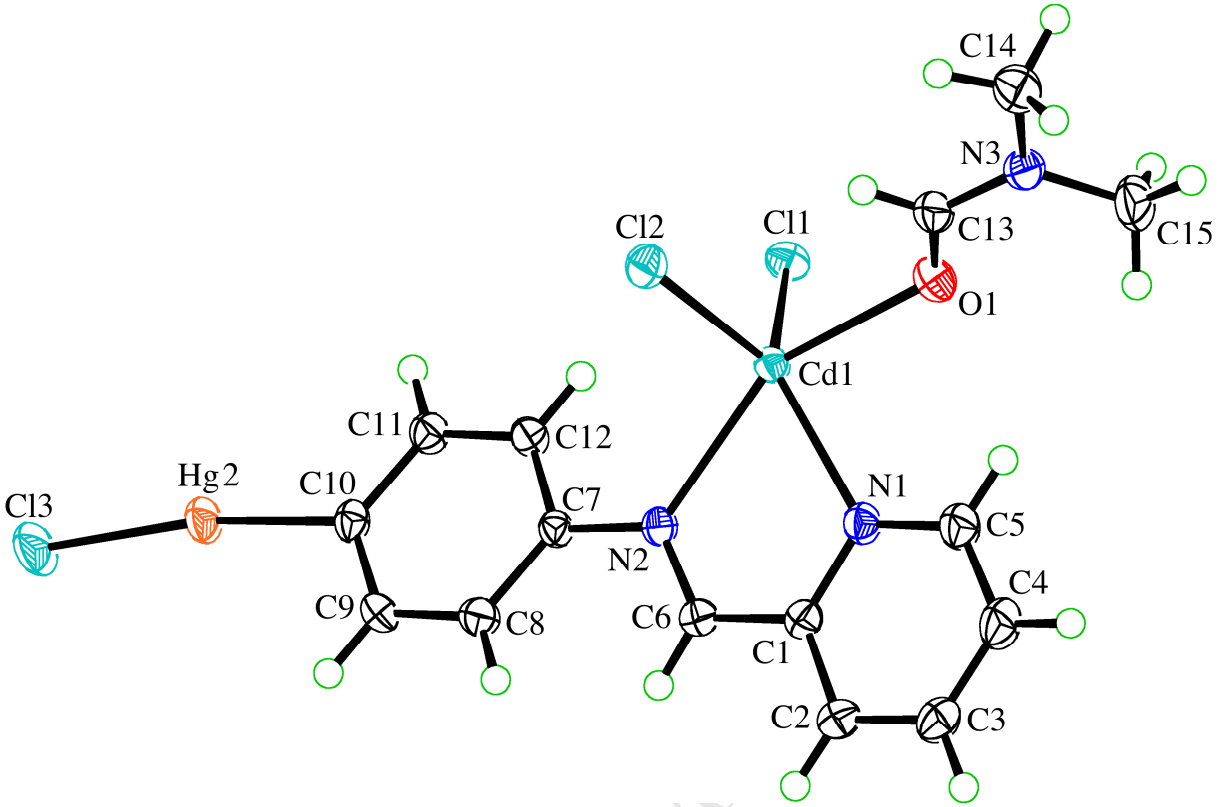

Fig. S3. The asymmetric unit of $(\mathbf{20})_n$ (50% probability ellipsoids).

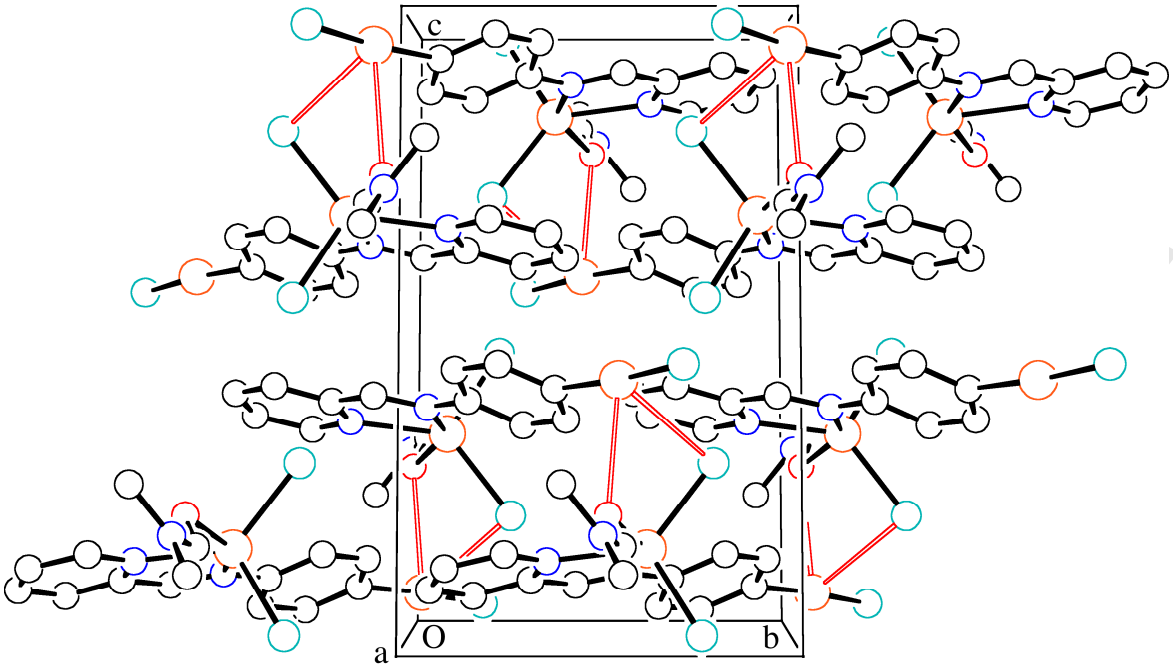

Fig. S4. The molecular packing of $(\mathbf{19})_n$.

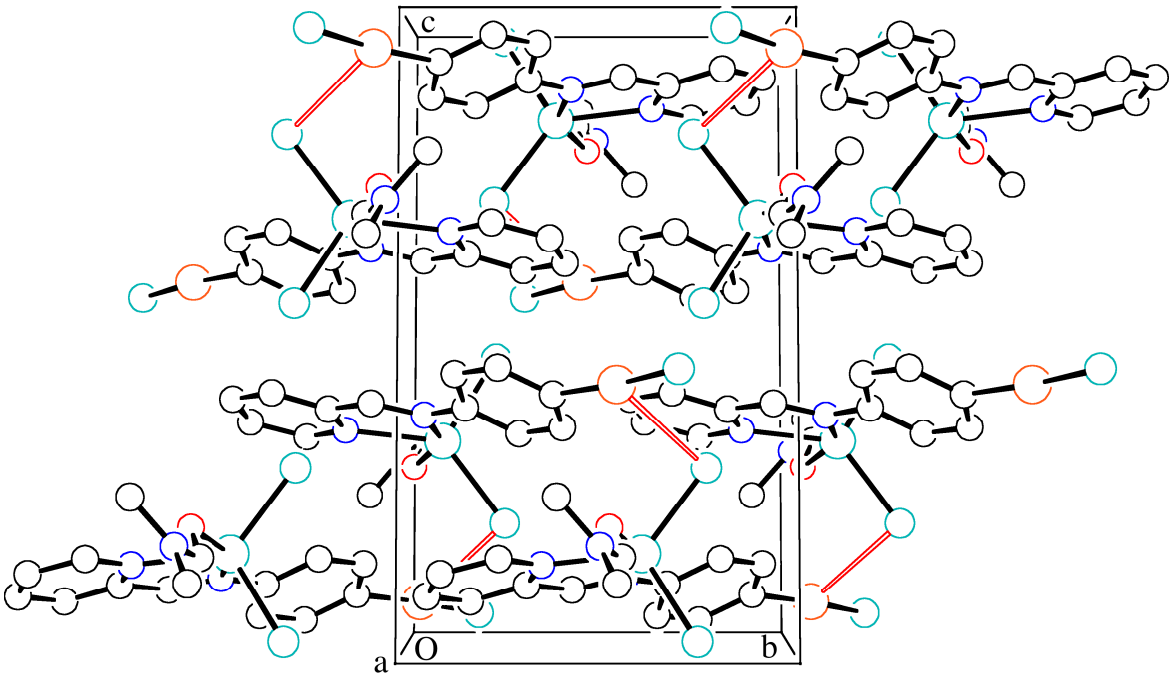

Fig. S5. The molecular packing of $(\mathbf{20})_n$.

Table S1.

Hydrogen bonding geometry (Å, º) for $(\mathbf{1})_n$[a]

D-H···A	D-H	H···A	D···A	D-H···A
N(1)-H(2)···O(1')	0.90(7)	2.36(7)	3.133(6)	144(6)
N(1)-H(1)···O(2'')	0.87(7)	2.21(7)	3.042(6)	161(6)

[a] Primed atoms refer to the molecule in the following symmetry related positions: '1$\frac{1}{2}$+*x*, $\frac{1}{2}$-*y*, -$\frac{1}{2}$+*z*; ''1-*x*, -*y*, 1-*z*

Table S2.

Hydrogen bonding geometry (Å, º) for $(\mathbf{3})_2$[a]

D-H···A	D-H	H···A	D···A	D-H···A
O(3)-H(3)···N(1)	0.85(9)	1.87(8)	2.589(6)	142(7)
O(4)-H(4)···O(2')	0.84	1.98	2.801(6)	167

[a] Primed atoms refer to the molecule in the following symmetry related positions: ' -*x*, -$\frac{1}{2}$+*y*, -$\frac{1}{2}$-*z*